

System-Wide Water Resources Program

Geomorphic Identification and Verification of Recent Sedimentation Patterns in the Woonasquatucket River, North Providence, Rhode Island

Maureen K. Corcoran March 2007



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Geomorphic Identification and Verification of Recent Sedimentation Patterns in the Woonasquatucket River, North Providence, Rhode Island

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Final report

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Abstract: The Woonasquatucket River in North Providence, RI, is a postglacial river flowing approximately 18 miles from its headwaters in North Smithfield, RI, to Providence, RI, where it joins the Moshassuck River and enters the Providence River. In 1776, a powder mill was constructed along the river to support the Colonies' efforts in the American Revolutionary War. The powder mill exploded in 1779, sending tons of gunpowder into the river. Subsequently, with the onset of the American Industrial Revolution in the early 1800s, the river also proved an ideal setting for textile mills. Because the mills operated machinery by waterpower, the river was directed into raceways that flowed through the mills. Dams were strategically placed on the river to aid in the diversion. Mill ponds that formed in response to the obstruction substantially altered sedimentation patterns and depositional features.

This research studies a section of the Woonasquatucket River in North Providence to assess the impact of these developments on the sediment regime. By using ²¹⁰Pb and ¹³⁷Cs, accepted methods of radioisotope dating used primarily in lacustrine and marine environments, a geochronology of sedimentation is established. However, because the mills predate the validity of these methods (approximately 150 years before present), other sediment dating techniques are needed to establish a geochronology of events prior to mill construction.

Elemental sulfur and potassium nitrate, components of gunpowder, were analyzed in the sediment to determine a historic timeline prior to the nineteenth century. Although soils at the site of the powder mill contain unusually high levels of sulfur, samples taken in areas away from the effects of the powder mill explosion also reveal high elemental sulfur levels. Pollen analysis focusing on the Japanese knotweed, *Polygonum cuspidatum*, an ornamental plant introduced in New England in the mid-1800s, is successfully used in this research as a stratigraphic event marker. These methods, coupled with a geomorphic framework, provide a significant insight into addressing sedimentation patterns in this and other riverine environments.

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Preface

This research describes geomorphic features of the Woonasquatucket River, RI, and investigates applicability of radioactive isotopes, ²¹⁰Pb and ¹³⁷Cs, in a fluvial environment. Innovative sediment tracers, sulfur and Japanese knotweed, are also used in this study to build a geochrononology of sediment deposition. The research was conducted by the U.S. Army Engineer Research and Development Center (ERDC), Geotechnical and Structures Laboratory (GSL), for the System-Wide Water Resources Program (SWWRP), U.S. Army Corps of Engineers, New England District, and the U.S. Environmental Protection Agency, Region I. Dr. Steven L. Ashby was Program Manager of SWWRP.

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COL Richard B. Jenkins was Commander and Executive Director of ERDC. Dr. James R. Houston was Director.

Unit Conversion Factors

Multiply	Ву	To Obtain
acres	4,046.873	square meters
acre-feet	1,233.5	cubic meters
angstroms	0.1	nanometers
atmosphere (standard)	101.325	kilopascals
bars	100	kilopascals
British thermal units (International Table)	1,055.056	joules
centipoises	0.001	pascal seconds
centistokes	1.0 E-06	square meters per second
cubic feet	0.02831685	cubic meters
cubic inches	1.6387064 E-05	cubic meters
cubic yards	0.7645549	cubic meters
degrees (angle)	0.01745329	radians
degrees Fahrenheit	(F-32)/1.8	degrees Celsius
fathoms	1.8288	meters
feet	0.3048	meters
foot-pounds force	1.355818	joules
gallons (U.S. liquid)	3.785412 E-03	cubic meters
hectares	1.0 E+04	square meters
horsepower (550 foot-pounds force per second)	745.6999	watts
inches	0.0254	meters
inch-pounds (force)	0.1129848	newton meters
kilotons (nuclear equivalent of TNT)	4.184	terajoules
knots	0.5144444	meters per second
microinches	0.0254	micrometers
microns	1.0 E-06	meters
miles (nautical)	1,852	meters
miles (U.S. statute)	1,609.347	meters
miles per hour	0.44704	meters per second
mils	0.0254	millimeters
ounces (mass)	0.02834952	kilograms
ounces (U.S. fluid)	2.957353 E-05	cubic meters

Multiply	Ву	To Obtain
pints (U.S. liquid)	4.73176 E-04	cubic meters
pints (U.S. liquid)	0.473176	liters
pounds (force)	4.448222	newtons
pounds (force) per foot	14.59390	newtons per meter
pounds (force) per inch	175.1268	newtons per meter
pounds (force) per square foot	47.88026	pascals
pounds (force) per square inch	6.894757	kilopascals
pounds (mass)	0.45359237	kilograms
pounds (mass) per cubic foot	16.01846	kilograms per cubic meter
pounds (mass) per cubic inch	2.757990 E+04	kilograms per cubic meter
pounds (mass) per square foot	4.882428	kilograms per square meter
pounds (mass) per square yard	0.542492	kilograms per square meter
quarts (U.S. liquid)	9.463529 E-04	cubic meters
slugs	14.59390	kilograms
square feet	0.09290304	square meters
square inches	6.4516 E-04	square meters
square miles	2.589998 E+06	square meters
square yards	0.8361274	square meters
tons (force)	8,896.443	newtons
tons (force) per square foot	95.76052	kilopascals
tons (long) per cubic yard	1,328.939	kilograms per cubic meter
tons (nuclear equivalent of TNT)	4.184 E+09	joules
tons (2,000 pounds, mass)	907.1847	kilograms
tons (2,000 pounds, mass) per square foot	9,764.856	kilograms per square meter
yards	0.9144	meters

1 Introduction

Background

The American Industrial Revolution was a catalyst for development of textile mills along the Woonasquatucket River in North Providence, RI (Rhode Island Historical Preservation and Heritage Commission 1981). Raceways and dams were used to divert the river into the mills for machinery operation. Reservoirs were constructed upstream to provide water to the mills during times of drought. Unfortunately, 200 years of industry situated along its banks contaminated the river with dioxin, heavy metals, polychlorinated biphenyls (PCBs), and other industrial pollutants (Stabler 1908, United States Environmental Protection Agency 1999).

Woonasquatucket is a Native American word, which when translated to English means "as far as the tidewater flows" (Wright et al. 1982). As implied by its name, the Woonasquatucket River is tidally influenced to Olneyville, RI. The Woonasquatucket River flows approximately 18 miles from its headwaters at Primrose Pond, near the town of North Smithfield, RI, to Providence, RI, where it joins the Moshassuck River and enters the Providence River (Figure 1).

Location of project

The United States Environmental Protection Agency (EPA) has designated a section of the Woonasquatucket River, the Centredale¹ Restoration Project. The Centredale Restoration Project is defined as the section of the Woonasquatucket River from the mill village of Centerdale south to the former Lyman Mill, and includes the former Allendale Mill. The area of interest of this study extends the boundary from Centerdale north to the former Greystone Mill. The Allendale and Lyman Mill dams and ponds formed by the dams are located within the study area outlined in Figure 1.

 $^{
m 1}$ Until 1893, the official spelling of the town was Centredale. In 1893, the United States Post Office required the use of Centerdale but local government continues to use Centredale. The spelling that appears on the United States Geological Survey topographic maps is Centerdale.

Purpose and scope

Based on sections of the Woonasquatucket River that are undeveloped, the river was once narrow and fast-flowing prior to textile mill development along its banks. Anthropogenic influence and natural events have possibly altered the geomorphic processes of the river. In order to understand the development of the Woonasquatucket River, which will provide valuable data to Federal and state agencies in environmental studies, sediment accumulation and geomorphic processes need to be addressed.

Previous research to establish a chronology using radioisotopes in lacustrine and marine environments provides a substantial base for applying these methods to mill ponds along the Woonasquatucket River. These methods, which have never been used in sediments along the Woonasquatucket River, provide a chronology of only the past 150 years. Additional dating horizons are needed to provide a chronology prior to the onset of the textile mills almost 200 years ago and to validate the radioisotope ages. In addition to radioisotopes, this research introduces elemental sulfur and nitrate, and Japanese knotweed (*Polygonum cuspidatum*), an invasive ornamental plant introduced in the mid-1800s, as possible dating horizons.

A powder mill was built on the Woonasquatucket River in 1776 to manufacture gunpowder for the Revolutionary War (Angell 1909). The mill exploded in 1779, sending tons of elemental sulfur, a component of gunpowder, into the river and adjacent floodplain. Because sulfur does not easily degrade, it should still be present in the soil and could serve as a useful time marker within the sediments.

Historic documents reveal that Japanese knotweed was introduced to the New England states in the mid- to late-1800s. The occurrence of Japanese knotweed post-dates the textile mills but the presence of its pollen may provide a useful tool for estimating the age of the sediment at a time prior to the ²¹⁰Pb capabilities of sediment age dating. Neither sulfur nor Japanese knotweed has been previously used as targets for constructing a chronologic sediment record.

The identification of geomorphic landforms, when combined with sediment age dating tools, enhances and improves site characterization and provides the scientific community a means of identifying and describing contaminated sites for optimal remediation and mitigation. For instance,

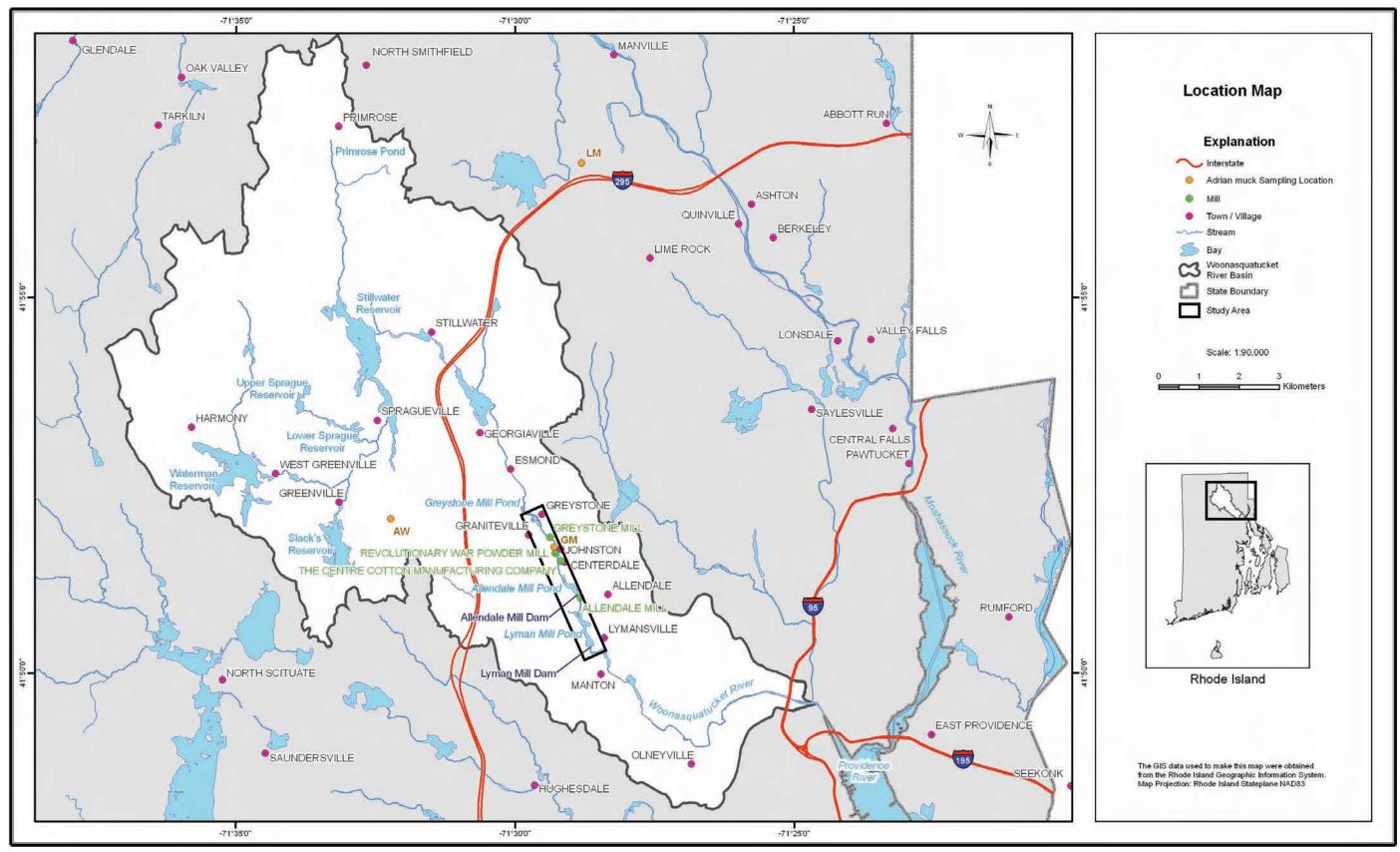


Figure 1. Location map of the study area, Woonasquatucket River, Rhode Island.

contamination is usually found in organic material and fine-grained sediment. By locating landforms with these kinds of material or sediment, contamination in the subsurface can be investigated more efficiently. Using these techniques advances geomorphology as a state-of-the art forensic geologic environmental tool in site characterization. This research also correlates anecdotal information about mill history.

2 Historical Significance of the Woonasquatucket River

Introduction

The Woonasquatucket River, because of its location in the heart of Colonial America, has a rich and important history. This section reviews events and actions of people occupying the area that lead to the development and condition of the river as it exists today. Historic events that played a key role in the evolution of the river include the American Revolutionary War, a war fought primarily between 13 North American colonies and Great Britain, and the Industrial Revolution, a time of innovative application of ideas with the subsequent development of water-powered mills along the Woonasquatucket River.

American Revolutionary War (1776-1784)

The area that later became the mill villages of North Providence, RI, was not the scene of any battle with the British during the American Revolutionary War, but the colony of Rhode Island still played a significant role in deciding its independence, and that of the 12 other colonies, from Great Britain. Until the summer of 1776, all gunpowder used in the colony of Rhode Island was secured from outside the colony, most of it coming from Groton and New London, CT, and was being transported to a magazine in Providence by boat or overland by horses or oxen (Angell 1909). It soon became apparent that a powder mill was needed in the colony of Rhode Island to supply the troops with a sufficient amount of gunpowder to fight the British.

In 1776, a powder mill was constructed on the west bank of the Woonas-quatucket River in Centerdale, Rhode Island (Figure 1). Angell (1909) described the location of the powder mill as being between the Centre Cotton Manufacturing Company Mill dam and a railroad station. Based on this description, local newspaper articles, and personal communication with Mr. Frank McGowan (2004), the Revolutionary War Powder Mill was once located on the west bank of the river, slightly downstream from the Greystone Mill on the east bank.

In 1779, the mill received a load of damp, unfit gunpowder to be remanufactured. A catastrophic explosion occurred during treatment of the gunpowder. The specific cause of the explosion is not known. The following is a newspaper article from the Providence Gazette, September 4, 1779, reporting the powder mill explosion.

Last Saturday Afternoon the Powder Mill in North Providence, with a Store adjacent, containing almost two Tons of Powder, were blown up. By this affecting Accident, two worthy Men lost their Lives, viz Mr. Jacob Goffe, and Mr. Laban Beverly, both of this Town, who expired the same Evening. It appears that they were employed in re-manufacturing a parcel of damaged Powder, which took Fire in one of the mortars, supposed to have been occasioned by a flint that was perhaps among it when it was returned to the mill; the flame was instantly communicated to a Quantity of Saltpetre and Sulphur, and then to the finished Powder, which unhappily had not been removed to the Building provided to receive it. The explosion was heard several Miles round, and a beam of the Mill was thrown about three Quarters of a Mile from the spot where it stood.

As evident from the article, the explosion was horrific and the amount of stored gunpowder significant. Gunpowder traces within sediment deposited during this time can provide modern clues as to the history of sedimentation and landform changes. The entire mill was demolished and never rebuilt. In 1786, the land was sold and a grist mill, a mill used for grinding grain, was built and operated until 1797.

American Industrial Revolution (1793)

Samuel Slater is credited with implementing the first water power mill in America thus beginning the industrial era in America (Haley 1939). In 1793, Slater began the American Industrial Revolution by converting an existing cotton mill along the Blackstone River in Pawtucket, RI, from operating with spinning jennies to the Arkwright system, spinning frames modeled on those by an English inventor, Richard Arkwright.

Mill construction in North Providence (1807-1823)

Reconstruction of the history of mill development along the Woonasquatucket River revealed human influences on the river and aids in understanding the response of the river to these modifications and its subsequent recovery. It is essential to understand the types of industry and the role each one played in shaping the river to better understand the evolution of the river morphology.

Textile mills were limited in size by the amount of water that could be obtained to operate the machinery. Raceways were constructed of drystone masonry to divert water through a water wheel with gates controlling the flow of water into the raceway. Individual machines were powered by the vertical main drive shaft of the water wheel, which was driven by power transmitted by horizontal line shafting mounted on the underside of the mill's ceiling beams. This meant that the first factories were necessarily kept short in length because the cumbersome line shafting and pulley system was too inefficient to permit otherwise (Sande 1975).

According to Skemp (1985), the Honorable Zachariah Allen made considerable improvements on power transmission in the late 1830s. His refined iron shaft and pulley system, known as "The American System of High-Speed Belting," proved considerably lighter and faster, improving from 50 to 200 rotations per minute (rpm) initially and later to 600 rpm (Skemp 1985). This proved much more efficient and allowed the same water wheel to distribute power over greater distances.

Lyman Mill (1807)

In 1807, Judge Daniel Lyman and others bought a privilege on the Woonasquatucket River and erected Lyman Mill (Sherman 1865). At the time of its establishment, it was the only mill of its kind in the country, selling and delivering goods directly from the factory to the consumer, conducting all of the processes from raw wool to the finished cloth (The Observer 1975). Lyman Mill holds the distinction as the first mill in Rhode Island to use the Scotch loom, a reproduction of a power loom used in Europe, and was also the first mill in the United States to produce worsteds, a yarn made from long wool fibers, on a power loom.

The Scotch loom failed in its initial test but Judge Lyman was not deterred. He employed Mr. David Wilkinson, known as an inventive

genius, to repair the loom. Mr. Wilkinson was successful and, in 1817, the loom was perfected and a new era in textile manufacturing began. From the successful introduction of this machine were laid the foundations of thousands of enterprising and thriving manufacturing villages that are scattered within the borders of New England (Wright 1878).

The Centre Cotton Manufacturing Company (1812)

In 1812, a cotton mill, operating under the name of the Centre Cotton Manufacturing Company, was erected by Mr. Israel Arnold on the site of a former sawmill and grist mill. Because previous mills already had used the river to operate, a dam and pond were already in place. The cotton mill started as a small building, 18×57 ft and two stories high, but after the successful introduction of the Scotch loom at Lyman Mill, an addition of 25×45 ft was added to accommodate about a dozen looms (Angell, 1909). The mill was deemed moderately successful in comparison with other mills operating during this time (Angell 1909). The success of the mill attracted other business and a village was soon established. The village, first known as Centre, is the present day Centerdale.

In 1823, Mr. Arnold sold half of his mill interest to Mr. Richard Anthony and, in 1826, released the remaining interest to Mr. James Anthony, son of Mr. Richard Anthony. Under the management of the Anthonys, the mill thrived. Additional buildings were constructed and the mill expanded to house 50 looms. The Anthonys are also credited with building the first store and church in Centerdale (Angell 1909).

In 1838, the mill was sold to Mr. Joseph Cunliff. On the night of March 17, 1850, a fire was discovered in one part of the mill and soon the whole structure was in flames (Angell 1909). The mill was completely destroyed but, in 1853, Mr. Cunliff rebuilt the mill. Because Centerdale relied so heavily on the mill, the construction of the second mill probably saved the town from total decay.

The cotton mill changed owners many times over the late 1800s. Production continued to improve and, in 1888, the looms were removed and machinery was installed for making warps, a yarn that is arranged lengthways on a loom and crossed by the woof or filling in a woven fabric for the mill at Dyerville, RI, where all the weaving was to be done.

Unfortunately, on August 7, 1889, fire broke out again in the upper story of the mill; but by the aid of a detachment of the Providence fire department, which responded to a call for aid, the mill was saved from destruction but was damaged to a considerable extent (Angell 1909). Repairs to the mill were made and the mill was once again in production. Cotton was no longer profitable to produce so in 1890, machinery was installed for the manufacture of worsted yarn and the mill became known as the Centerdale Worsted Mill and the mill increased to about three times its former size.

In 1940, the Atlantic Chemical Company replaced yarn manufacturing with chemical production at the Centerdale Worsted Mill site. Various chemical activities continued until the early 1970s, when a fire destroyed most of the structures at the mill site (United States Environmental Protection Agency 2005). Two apartment complexes, Brook Village, constructed in 1977, and Centredale² Manor, built in 1982, now occupy the site.

Greystone Mill (1813)

Greystone Mill was built as a cotton mill in 1813; a year after the Centre Cotton Manufacturing Company mill was constructed. Cotton yarn and cloth were produced until 1835, when the mill was used by various owners to produce yarn, paper, grain, and wool shoddy (reprocessed wool). Greystone Mill was burned and rebuilt twice, in 1872 and 1877. With the exception of a business occupying several offices, the mill is now in ruins and sections of the raceway are no longer apparent, likely filled in by natural events (Kulik and Bonham 1978).

Allendale Mill (1822)

Within the study area, the most prominent mill is Allendale Mill constructed in 1822 by Zachariah Allen. The mill is historically significant in its design and manufacturing history. A distinctive, dormered roof caps the four-story stone rubble structure with a stepped gable on the north side of the building.

In the Allendale Mill, Mr. Allen installed the first power loom in the United States for the making of wool broadcloth, a fabric made entirely of

² The building uses the local accepted spelling of Centredale.

wool. According to Kulik and Bonham (1978), the mill is historically noteworthy as the first mill to use the power loom for manufacturing broadcloth and also the first mill to use a rolling process, called calendaring, to impart a gloss finish to cloth. Although the purpose of the mill was to produce broadcloth, mill operations changed in 1839 to produce cotton fabric (Bicknell 1920) to compete with cotton mills in the southern United States.

Mr. Allen introduced innovative fire-prevention features later adopted in new mill construction. The Allendale Mill incorporated the first heavy fire doors, sprinkler system, rotary fire pump, and copper-riveted fire hose to be used in American textile mills (Rhode Island Historical Preservation Commission 1981). When the company insuring Mr. Allen's mill did not reward his endeavors by giving him a reduced rate, he formed his own insurance company, Manufacturers Mutual Fire Insurance Company. Ironically, in 1878, a fire started in the attic of the Allendale Mill and the mill suffered substantial damage from water used to contain the fire.

On May 7, 1973, the Allendale Mill was approved for placement on the National Register of Historic Properties. The mill produced textiles until 1976 (Kulik and Bonham 1978) and was then used for a variety of manufacturing and commercial purposes. In 1993, the mill was renovated and converted to condominiums, now known as the Mill at Allendale Condominiums.

Reservoir construction for the mills

Dams were set in place to pond water near the mill headrace, a canal diverting water from the pond to flow through the water wheel. Ponds formed by the dams at Allendale Mill and Lyman Mill are referred to as Allendale Mill Pond and Lyman Mill Pond, respectively. The river has a fall of approximately 7.0 ft at Centerdale, about the same at Allendale, and approximately 10 ft at Lymansville (Bayles 1891).

The Allendale Mill Dam, built to direct water from the river to operate machinery at Allendale Mill, was likely constructed in 1822, the same year as the mill was built. The 8×106 -ft timber and earth dam breached on November 26, 1991, because of rotted wood, turning a section of the Woonasquatucket River into a broad mudflat (Salit 2001). The historic dam could not be saved. In 2001, a new 13-ft-high concrete dam was built as a replacement (Salit 2001).

Mills along the river depended on the water to power the machinery so during times of drought the mills became idle. In 1822, a group of Woonasquatucket Valley mill owners, led by Mr. Allen, formed a corporation to ensure an adequate supply of water through the construction of reservoirs (Rhode Island Historical Preservation Commission 1992). A charter, the first one awarded in the United States for making reservoirs for hydraulic purposes, was obtained by the corporation to construct reservoirs for retaining floodwaters to use to operate machinery during times of drought.

The first industrial reservoir, Greenville Reservoir (Slack's Reservoir), to support the mills on the Woonasquatucket River was completed in 1822. The Sprague Lower and Upper reservoirs followed it in 1827 and 1836, respectively. The Waterman Reservoir was in use by 1838 and in 1853, the Stillwater Reservoir was added to the system (Rhode Island Historical Preservation Commission 1992) (Figure 1).

Recognition of the Woonasquatucket River (1990s)

In 1992, the city of Providence, the Rhode Island state government, the academic community, and the private sector jointly formed a non-profit organization referred to as the Providence Plan. The mission of the Providence Plan is to restore hope and create new opportunity for the people of Providence through a comprehensive initiative designed to address the fundamental causes of poverty and urban decline (The Providence Plan 2005).

In 1994, recognizing the historic significance and beauty of the river, the Providence Plan began a revitalization of Providence known as the Woonasquatucket River Greenway Project using the Woonasquatucket River as the focal point. Along the river, the Greenway Project will include a bicycle/pedestrian path, recreational areas, green spaces, and will also promote restoration of historic industrial sites. At this time, the Greenway Project is downstream of the proposed study site, but influence of the project will impact the entire river by promoting environmental awareness of the Woonasquatucket River.

In March 1998, Vice President Al Gore designated the State of Rhode Island and the Woonasquatucket River Greenway as one of 16 Brownfields Showcase Communities (State of Rhode Island and Providence Plantations 2002). The United States Environmental Protection Agency (2002a) defines a brownfield site as being, with certain legal exclusions and

additions, real property, the expansion, redevelopment, or reuse of which may be complicated by the presence or potential presence of a hazardous substance, pollutant, or contaminant. A brownfield site contains buildings or land previously developed but no longer occupied. These areas have been damaged by previous development but are considered suitable for redevelopment. Brownfields Showcase Communities have three main goals: promote environmental protection, economic redevelopment and community revitalization through the assessment, cleanup and sustainable reuse of brownfields; link Federal, state, local, and non-governmental action supporting community efforts to restore and reuse brownfields; and develop national models demonstrating the positive results of public and private collaboration addressing brownfield challenges (United States Environmental Protection Agency 2003).

President Bill Clinton, in his 1997 State of the Union Address, recognized the historical and environmental significance of rivers in the United States and also the efforts of residents to restore their watersheds by introducing the idea of American Heritage Rivers..... "Tonight, I announce that this year I will designate 10 American Heritage Rivers, to help communities alongside them revitalize their waterfronts and clean up pollution in the rivers, proving once again that we can grow the economy as we protect the environment." The American Heritage Rivers initiative is an innovative response to help river communities that seek Federal assistance and other resources to meet some tough challenges (United States Environmental Protection Agency 2002b). Without any new regulations on private property owners, state, local and tribal governments, the American Heritage Rivers initiative attempts to make more efficient and effective use of existing Federal resources, reducing bureaucratic obstructions, and assisting cleanup of the Woonasquatucket River (United States Environmental Protection Agency 2002b).

In 2000, the United States Environmental Protection Agency named the Centredale³ Restoration Project to the National Priorities List (NPL) of hazardous waste sites, making it eligible for additional Federal Superfund cleanup funds (United States Environmental Protection Agency 2002c). In response to the Superfund designation, the United States Environmental Protection Agency and the U.S. Army Engineer District, New England, are conducting an investigation on the spatial extent of dioxin, a group of

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 $^{^3}$ The United States Environmental Protection Agency and the United States Army Corps of Engineers, New England District, use the local spelling of Centredale.

industrial by-products harmful to fish and wildlife, along the Woonasquatucket River. This investigation is in the initial stage of a feasibility study that will be used to evaluate remediation methods for restoring the Woonasquatucket River.

3 Geology of the Woonasquatucket River

Introduction

The Woonasquatucket River displays characteristics of a fluvial system but, although a post-glacial river, was also greatly influenced by glacial activity. Glacial and fluvial influences control the river channel and provide limits for its adjustment in response to flood events, dams and raceways, and reservoir control. Geomorphic features change in accordance with river adjustments.

This section discusses the glacial history, geomorphic responses, and streamflow analyses of the Woonasquatucket River.

Glacial history

The focus on glacial investigations in Rhode Island has been in the southern part of the state where Block Island, which lies approximately 75 miles south of Providence, Rhode Island, defines the limits of glacial advancement as a terminal moraine (Figure 2). The New England region was glaciated at least once, and perhaps several times, during the Pleistocene Epoch (Smith 1956) (Stone et al. 1986) as evident from numerous glacial deposits on Block Island. Smith (1956) suggested that perhaps more than one glacial event occurred in the Providence area but that earlier glacial deposits are not exposed, were removed by succeeding ice sheets, or are present but not distinguishable from later drift. Based on correlated ice-margin positions, the recession of the Late Wisconsin Laurentide ice sheet through the North Providence area occurred between 17,000 and 16,000 years before present (BP) (Boothroyd et al. 1998).

The Woonasquatucket River is entrenched in a valley train, a glacial feature described by Smith (1956) as graded outwash deposited by glacial streams, which fills a valley bottom from wall to wall. The valley train is derived primarily from crystalline rock and, because the rock has been transported a considerable distance, consists of well-rounded grains.

The outwash plain, consisting of sand and coarse gravel deposits, extends the length of the Woonasquatucket River and diverts the southern part of the river to flow in an eastern direction instead of a continuing

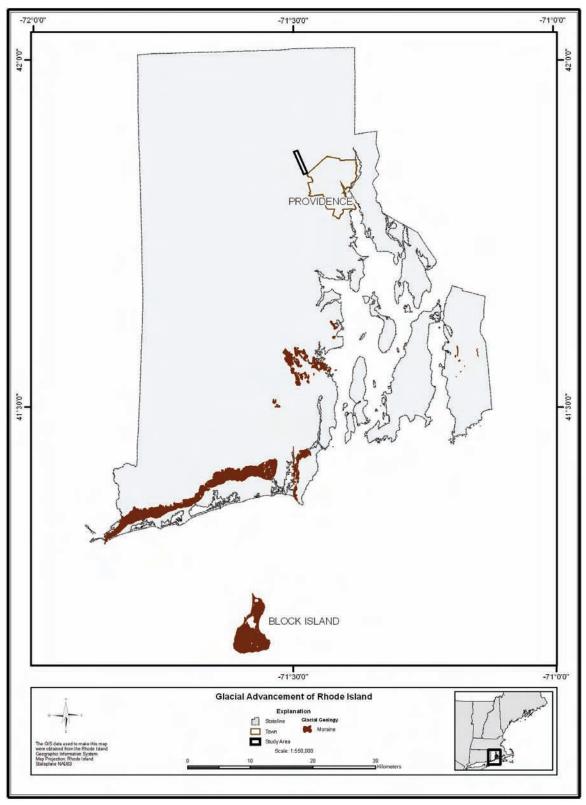


Figure 2. The limits of glacial advancement defined by Block Island, a terminal moraine (modified from Boothroyd et al. 1998).

southeastward course. Because of the deep entrenchment, the elevated outwash plain is sometimes mistakenly interpreted as river terraces deposited by fluvial activity (Smith 1956).

Surficial geology

Krinsley (1949) published the only map of the surficial geology of this area. Krinsley's work and that of J. Hiram Smith were the basis for the United States Geological Survey's Geologic Quadrangle 84, the surficial geologic map for the Providence 7.5 min quadrangle published in 1956.

Surficial deposits in this area are predominantly of glacial origin and can be classified broadly as glacial till (Figure 3). Glacial till, mapped by Krinsley (1949) and Smith (1956) as ground moraine, is from either of two sources depending on the bedrock from which it was derived—one consisting primarily of material derived from sedimentary rocks of Pennsylvanian age and the other consisting of crystalline rock of Paleozoic and Precambrian age.

According to Smith (1956), the stratified drift exists as outwash plains, kame terraces, kame plains, kames, and ice-channel fillings. The remainder of the surficial material along the Woonasquatucket River is alluvium deposited when the river overtops its banks. The alluvium, mapped as floodplain or alluvial deposits, is reworked glacial outwash, floodplain deposits, and river terrace. The river terraces are former floodplain deposits and are, therefore, considered depositional features.

Bedrock geology

The bedrock underlying the surficial deposits consists of Pennsylvanian sandstone, shale, and conglomerate of the Narragansett Basin and older igneous and metamorphic rocks surrounding the basin (Smith 1956). As shown in Figure 4, the bedrock in the vicinity of Allendale Mill and Lyman Mill consists of sedimentary rocks of Paleozoic age. In the Greystone Mill area, the bedrock is crystalline rock of Precambrian age.

Geomorphology of the Woonasquatucket River

Methodology

Historic aerial photography, United States Geological Survey topographic quadrangles, journal articles, and field investigations were used in the

geomorphic study to identify morphological features and changes along the river. Environmental Systems Research Institute (ESRI) ArcView 8.3 was used to develop a Geographic Information System (GIS) for the study site to manage data, produce computations for the streamflow analysis, and provide a comparative display of data. A description of each dataset and its use is detailed in the following sections.

Aerial photography

EarthData International

Aerial photography from several sources was obtained for this study (Table 1). The photography was scanned and saved in a tagged image file format (.tif) to import into the GIS.

Date Approximate Scale Source Flown 10/26/1951 1 in. = 1,690 ft United States Army Corps of Engineers, New England District 1 in. = 2,000 ft United States Geological Survey (USGS) 5/19/1955 5/1/1956 1 in. = 2,420 ft National Ocean Survey (NOS) Aerial Viewpoint (AVPT) 2/7/1962 1 in. = 1,320 ft Aerial Viewpoint (AVPT) 9/2/1963 1 in. = 1,710 ft Agricultural Stabilization and Conservation Service (ASCS) 9/2/1963 1 in. = 1,710 ft 3/9/1970 1 in. = 2,000 ft United States Geological Survey (USGS) 1976 Col-East, Inc. 1 in. = 530 ft National Ocean Survey (NOS) 9/20/1979 1 in. = 2,510 ft 1 in. = 2,070 ft United States Geological Survey (USGS) 3/18/1981 National Ocean Survey (NOS) 8/23/1985 1 in. = 2,480 ft Rhode Island Geographic Information System (RIGIS) (USGS) 1992 1 in. = 467 ft 1995 Rhode Island Geographic Information System (RIGIS) (USGS) 1 in. = 467 ft Rhode Island Geographic Information System (RIGIS) 1997 1 in. = 467 ft Col-East, Inc. 5/17/1995 1 in. = 530 ft

Table 1. Sources of aerial photography.

The aerial photography was rectified in Rhode Island State Plane (United States Survey Feet, NAD 83) using 1997 United States Geological Survey digital orthophotographic quadrangles (DOQs), purchased from the Rhode Island Geographic Information System (RIGIS). RIGIS is a consortium of government and private organizations employing computer and communications technology to manage a collective database of comprehensive geographically related information.

3/4/2000

1 in. = 400 ft

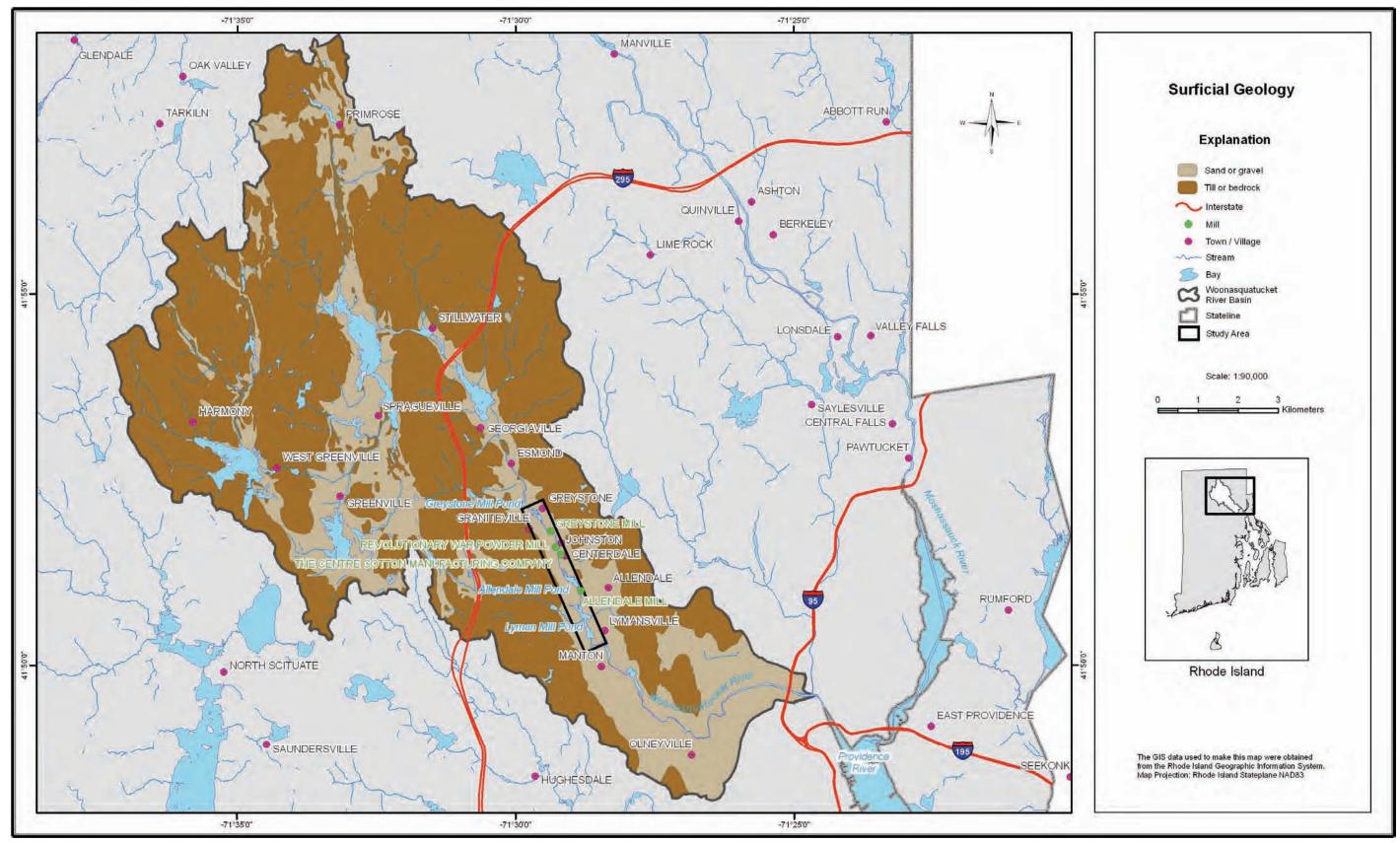


Figure 3. Surficial geology of the Woonasquatucket River Watershed (after United States Geological Survey 2005).

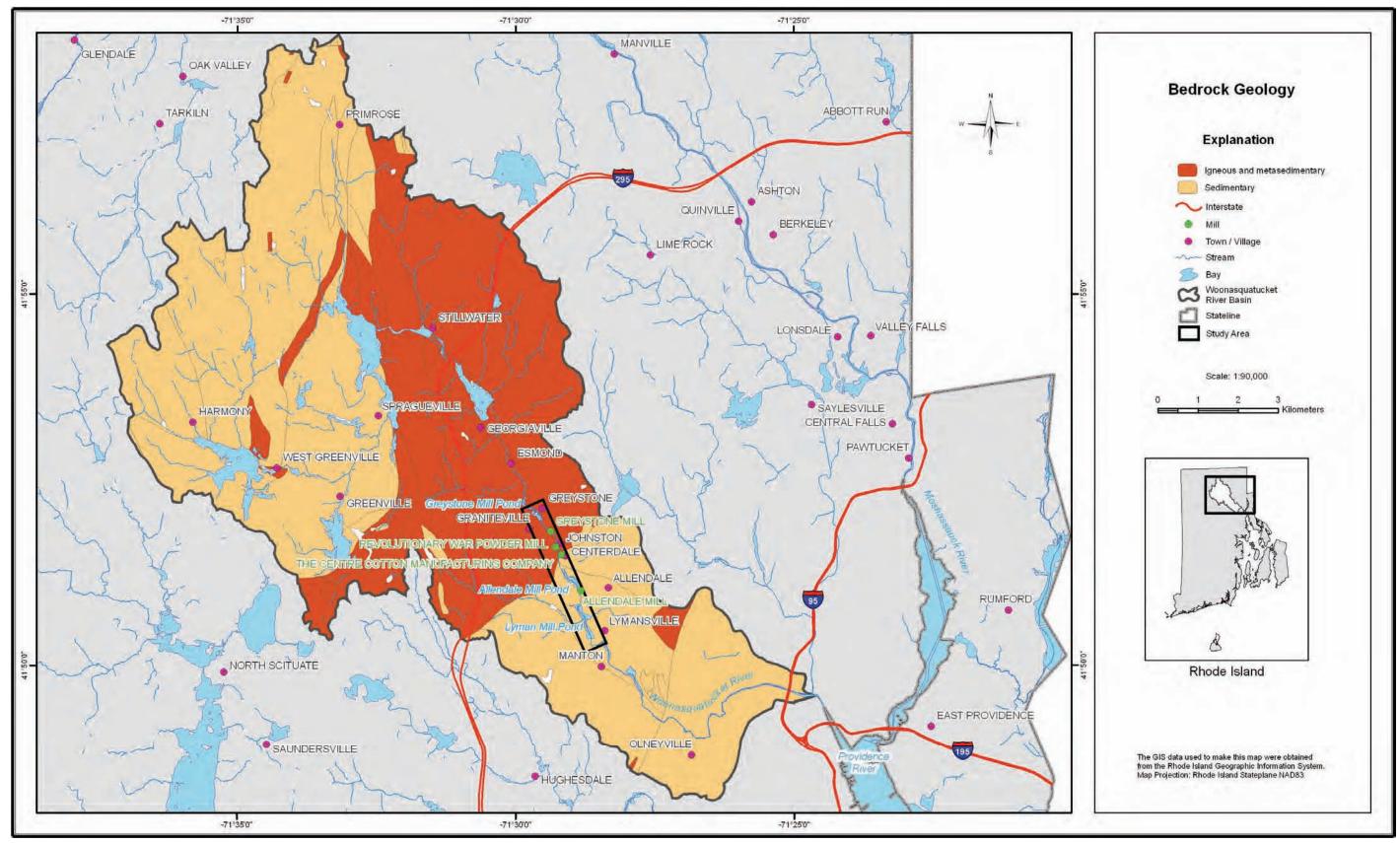


Figure 4. Bedrock geology of the Woonasquatucket River Watershed (after United States Geological Survey 2005).

The DOQs are used as a base for rectification because of the degree of accuracy in developing them. The relative scale on the ground for the DOQs is 1:5000, giving a map accuracy of 9.8 to 16.4 ft. However, rectification of the aerial photography to the DOQs proved inaccurate for tracing the river channel when using buildings and roads, landmarks usually used to select coordinates from the DOQs. Instead, points closer to the river had to be used to match individual images to each other.

Some of the photography could not be used in the study because of poor resolution or rectification problems. Unfortunately, the earliest photography available for this area (1935) is too poor a quality to be used in identifying river changes. The 1970 photography also presented a problem because of poor resolution.

Topographic quadrangles

Topographic maps are also essential when characterizing changes in the river morphology. Topographic quadrangles available for this site were purchased from the United States Geological Survey in Reston, VA, and scanned and rectified if pertinent to the Woonasquatucket River evolution (Table 2). An index map of the quadrangles is shown in Figure 5.

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Map Name	State	Scale	Survey Year	Revision Year	Publication Year
Burrillville	RI	62.5K	1888	Not Applicable	1940
Burrillville	RI	62.5K	1915	Not Applicable	Not Applicable
Georgiaville	RI	24K	1942	Not Applicable	1954
Georgiaville	RI	24K	1942	1970	1972
Georgiaville	RI	24K	1942	1975	1975
Pawtucket	RI	24K	1938	1949	1965
Pawtucket	RI	24K	1938	1970	1973
Pawtucket	RI	31K	1938	Not Applicable	1944
Pawtucket	RI	24K	1949	1975	1977
Providence	RI	62.5K	1887	Not Applicable	1939
Providence	RI	31K	1935	Not Applicable	1956
Providence	RI	24K	1935	1957	1959
Providence	RI	24K	1935	1970	1972
Providence	RI	24K	1957	1975	1978
Providence	RI	25K	Not Applicable	1981	1987
Providence	RI	100K	Not Applicable	1977	1984

Table 2. Topographic quadrangles of the Woonasquatucket River.

Soil survey maps

Soils reflect post-glacial development and are important in reconstructing the geochronology of the river (Appleby 2000, 2001). The Soil Survey of Rhode Island (United States Department of Agriculture 1981), published prior to the construction of Centredale Manor at the site of the former Centerdale Worsted Mill, and the 1996 digital soil survey map were used to assess the soil type and conditions surrounding the site. The digital soil survey map was obtained from the Natural Resources Conservation Service (NRCS), Soil Survey Geographic (SSURGO) Database Web site (United States Department of Agriculture 2005).

Subsurface sampling

To estimate the sedimentation rate of the river and trace the spatial distribution of the Woonasquatucket River deposits, 20 subsurface vibracore sediment samples were obtained in Allendale Mill Pond and 10 in Lyman Mill Pond during the first phase of sampling in May 2003 (Figure 6). Twenty additional vibracores in Lyman Mill Pond were recovered in a second phase of sampling in March 2005. The river channel at Greystone Mill could not be accessed so samples were taken along the floodplain using a pushprobe and 2.0-in. I.D. (internal dimension) polyvinyl chloride (PVC) pipe.

Selection of sample locations was based on several criteria: a preference for glacial and fluvial deposits (such as kame and alluvial deposits), depositional environment (abandoned channel), river morphology (historic and present), and river bathymetry. Other factors, such as the breaching of the Allendale Mill Dam, were also considered in selecting vibracore sites.

Because of possible contamination, vibracores for the Allendale Mill and Lyman Mill Ponds were slabbed and described in a secured site at the United States Environmental Protection Agency Atlantic Ecology Division (AED) in Narragansett, RI. The United States Environmental Protection Agency AED laboratory staff constructed a box to hold the core in place while using a circular cutoff saw to cut the core in half. The box was lined with plastic, which was replaced after each core was slabbed. Water was drained from each vibracore prior to slabbing. After the core was slabbed, it was placed on a table lined with paper then measured, described, and photographed.

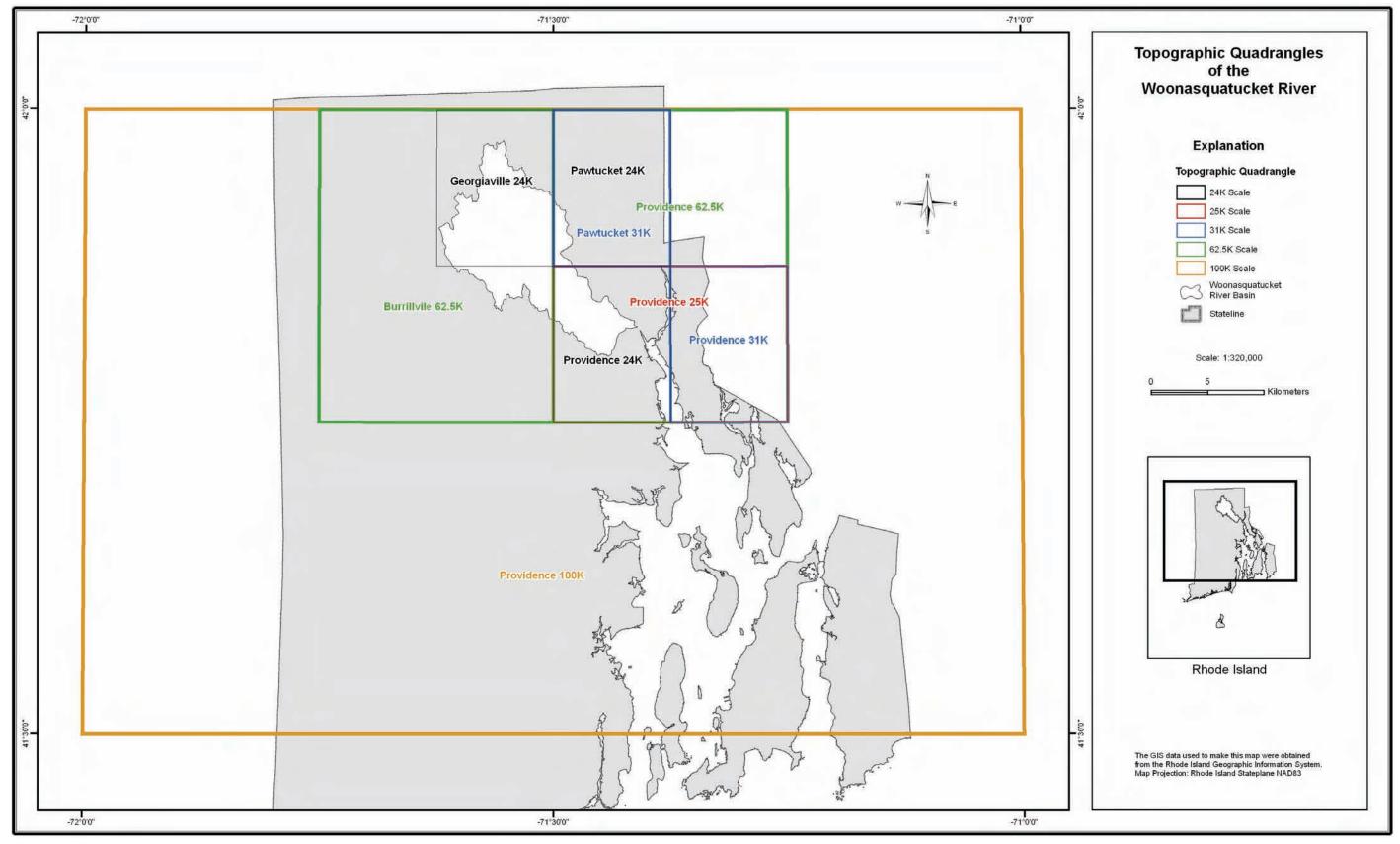


Figure 5. Topographic quadrangles of the Woonasquatucket River.

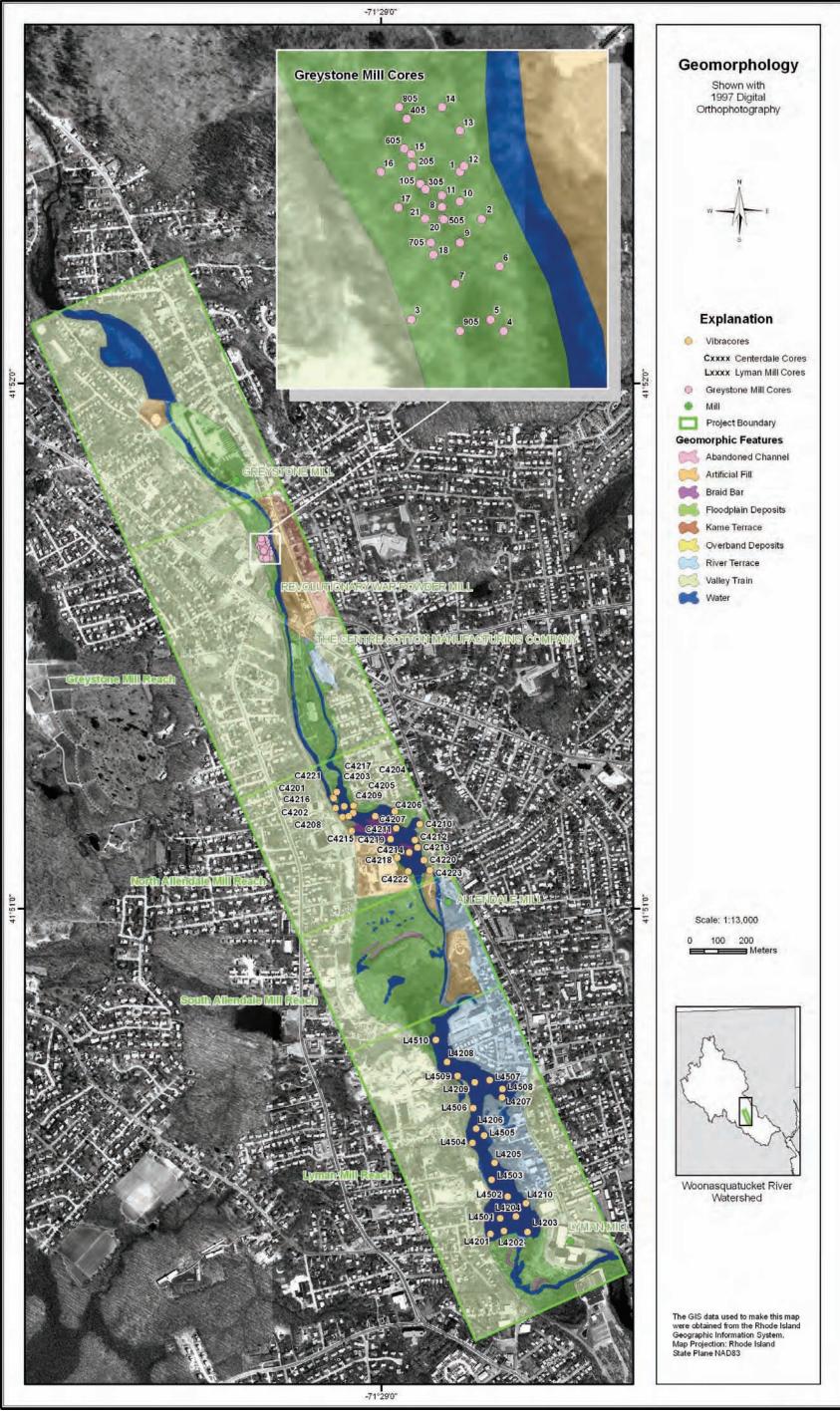


Figure 6. Geomorphology of the Woonasquatucket River, RI, based on field interpretation and Smith (1956).

Samples were selected based on changes in lithology. If the lithology was consistent throughout the core, the core was sampled in 0.8-in. increments. Plastic utensils were used to remove samples from the core and were disposed of after each sample was taken to prevent crosscontamination.

Samples were placed in glass jars and labels recording sample number, site, and purpose of sample were placed on the jars and secured with tape. The information on the labels was recorded on a chain-of-custody form. The samples were stored in coolers and placed in a refrigerated room outside of the laboratory. Samples were then shipped to the appropriate laboratory for analyses.

Historic channel geometry

A valley train, which formed as outwash deposits from a receding glacier, filled the Woonasquatucket River valley bottom (Smith 1956). The material deposited by the glacier consists almost entirely of eroded crystalline rock. Subsequently, the headwaters at Primrose Pond entrenched a channel in the outwash to produce the Woonasquatucket River.

Using aerial photography, the outline of the river was traced at 12 different years to identify major changes in the channel during this almost 50-year interval. Time intervals between successive outlines ranged from 1 to 8 years (Figure 7). These outlines show that the river is confined by the valley train and the ponds and also confirm the channel abandonment, identified by arrows in Figure 7, between 1970 and 1976 south of the Allendale Mill Dam.

Using the GIS, the length of the channel over the study site was measured from each year of the aerial photography in Figure 7. The total length of the Woonasquatucket River channel in the study area changed six percent between 1979 and 1987, but over the almost 50-year interval, the channel is essentially unchanged. As apparent from these measurements and the relative position of the channel, the deviation of the channel over time shows only minor variation. The measurements are shown beside the corresponding river channel in Figure 7. Because the Woonasquatucket River is entrenched in a valley train, the lack of erosive material in the valley train, and the minimal movement of the Woonasquatucket River channel, the ability of the river channel to maintain essentially the same course over a period of almost 50 years is attributed to the valley train.

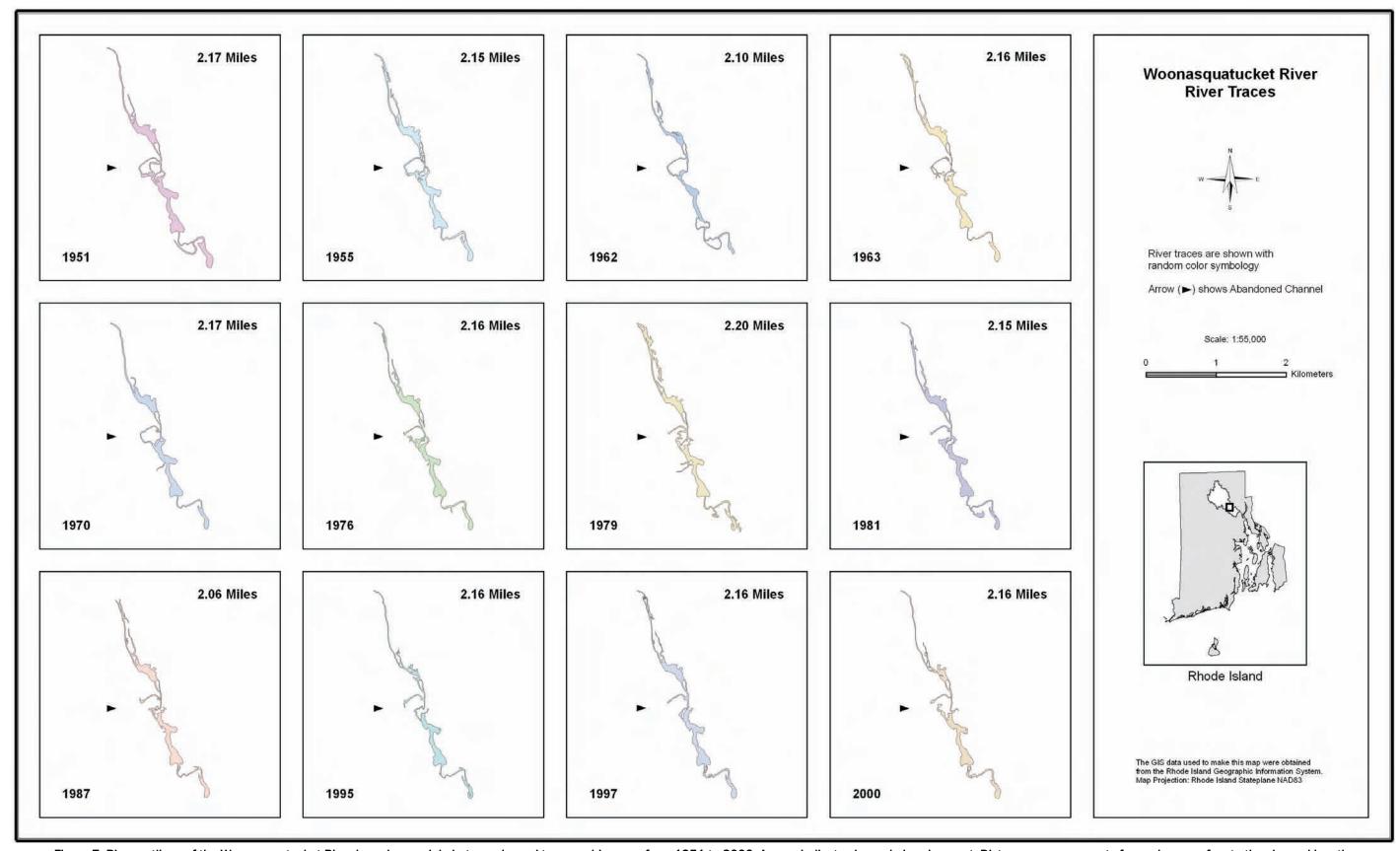


Figure 7. River outlines of the Woonasquatucket River based on aerial photography and topographic maps from 1951 to 2000. Arrows indicate channel abandonment. Distance measurements for each year refers to the channel length.

Geomorphic features

Geomorphic features identified are those typically found in riverine and glacial systems: braid bars, floodplain deposits, river terraces, abandoned channels, kame terraces, ground moraines, and valley train deposits.

A braid bar is indicative of a braided channel and is manifested as an island of sediment within a river channel. Braid bars of the Woonasquatucket River are apparent only after the Allendale Mill Dam breach and are not necessarily depositional features. Because of this, the river is not classified as a braided system.

Floodplain deposition occurs as sediment is deposited over the riverbanks. These deposits have an abundance of sand with lesser amounts of silt and clay. Organic layers are also present in these deposits from tree leaves and other small plant remains.

River terraces are either depositional or erosional (Ritter et al. 2002). The terrace along the east bank of the Woonasquatucket River is a former floodplain and based on Smith's (1956) field interpretation, is classified as a depositional river terrace. Lyman Mill and Allendale Mill are situated on this prominent river terrace above the recent floodplain of the river.

Abandoned channels are segments of channel abandoned by the river usually because of a river shortening its course by cutoffs. The abandoned channel is slowly filled with alluvium deposited by the river until the previous channel is disconnected from the flow of the river. Clayey sediments and organic matter, collectively referred to as channel-fill deposits, are deposited until filling is complete. During flooding, overbank deposits may still be introduced into the abandoned channel.

The study area has been divided into the following segments (Figure 6):

- Greystone Mill Reach, includes the area directly south of Greystone Mill and extends approximately 1,970 ft to the Centredale Manor site.
- North Allendale Mill Reach, extends south from the Centredale Manor site to the Allendale Mill.
- South Allendale Mill Reach, includes Allendale Mill and extends south to the north boundary of Lyman Mill Pond.
- Lyman Mill Reach, extends from the north boundary of Lyman Mill Pond to the raceway of Lyman Mill.

The geomorphic features (Figure 6) and the soils (Figure 8) are described in the following sections for each of the four segments.

Greystone Mill Reach

The former site of the Revolutionary War Powder Mill is situated on the west bank of the Woonasquatucket River and occupies an area covered by a valley train. Greystone Mill is located on the east bank, the opposite bank of the powder mill site. The Revolutionary War Powder Mill was destroyed in a 1779 explosion and the site is now occupied by several buildings. With the exception of a business located in the south part of the building, Greystone Mill is abandoned. Both mills diverted the water from the river into a raceway to operate mill machinery.

West bank of the Woonasquatucket River

The probable man-made river diversion constructed to operate the powder mill is apparent in the United States Geological Survey Geologic Quadrangle 84 and aerial photography (Figure 9). During intervals of high precipitation, water fills this suspected abandoned raceway. This area is mapped as a floodplain of the river on the west bank, directly south of Greystone Mill. The valley train lies west of the floodplain. Because the valley train was incised by the formation of the Woonasquatucket River, it gives the appearance of a river terrace. The elevated land surface from the river provided an ideal location for mills.

Floodplain deposits of sand and silt are evident on the west bank of the river but the overbank flow of the river presently does not appear to reach what is interpreted as the former raceway of the powder mill. Ice channel deposits, elongated ridges of sand and gravel laid down in channels in the ice or between ice blocks, lie within the valley train on the west bank (Smith 1956).

East bank of the Woonasquatucket River

The area directly south of the mill has been visibly excavated and used as a dumping site for construction material. Because of this disturbance, the east bank adjacent to the river is mapped as artificial fill but covers deposits of the valley train. A kame terrace lies east of the artificial fill (Figure 6) and because of its elevated position from the river, is highly urbanized with businesses and housing developments. The high kame terrace

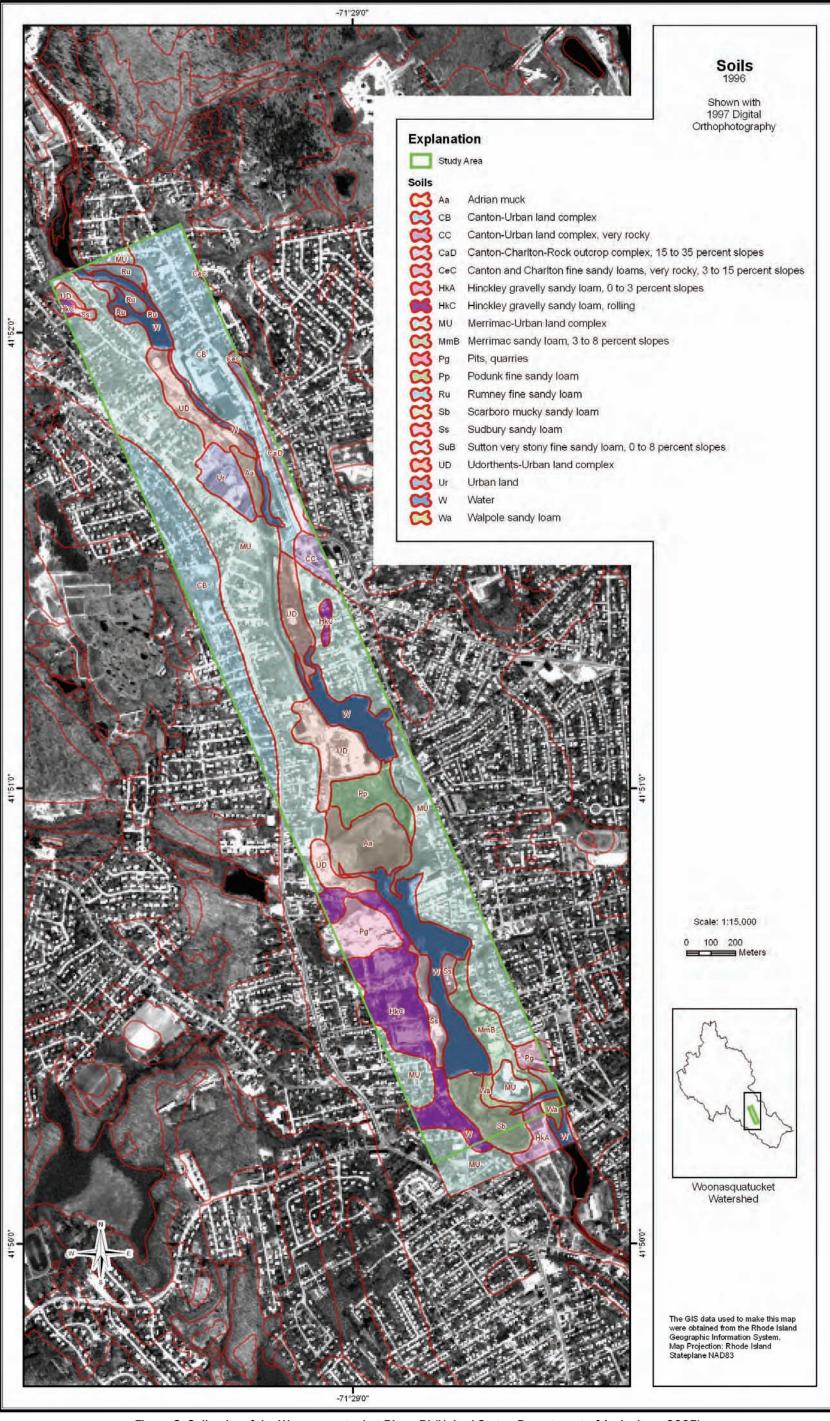


Figure 8. Soil units of the Woonasquatucket River, RI (United States Department of Agriculture 2005).

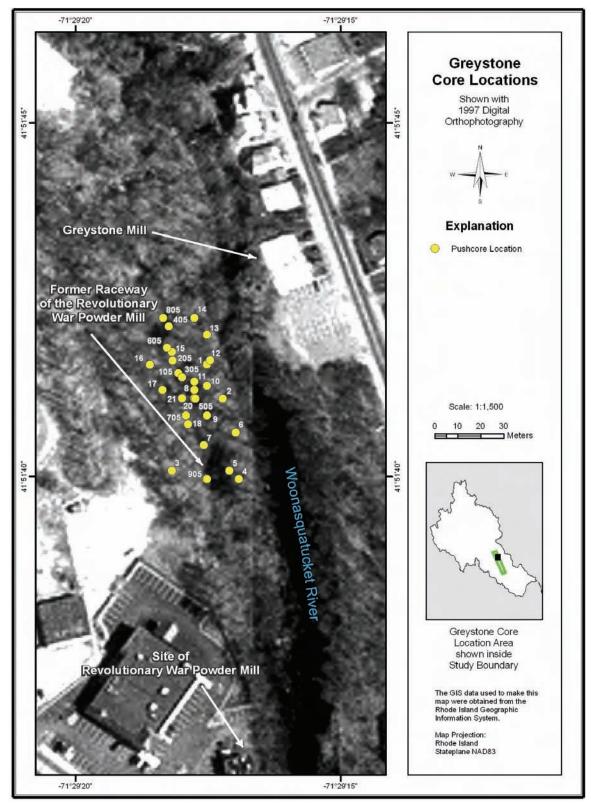


Figure 9. Digital orthophotograph of the Greystone Mill site.

between Greystone and Centerdale is approximately 30 ft above the adjacent valley train (Smith 1956). Smith (1956) identified the kame terrace as sand and gravel deposited by meltwater streams positioned between glacial ice remaining in the valleys and valley walls.

North Allendale Mill Reach

The North Allendale Mill Reach includes the site of the Centre Cotton Manufacturing Company Mill and extends south approximately 0.7 of a mile to the Allendale Mill. Because of the breaching of Allendale Mill Dam in 1991, the river channel between the Allendale Mill and the former Centre Cotton Manufacturing Company Mill appears significantly different than the same area in aerial photographs prior to 1991. As the dam breached and the water level subsided, more sediment was exposed in the Allendale Mill Pond. This sediment is evident in the 2000 aerial photography, giving the river the appearance of a braided channel. After the dam was rebuilt in 2001, the river returned to historic water levels and once again water covered the sediment.

East bank of the Woonasquatucket River

Based on aerial photography and topographic maps, the east bank of the river in the North Allendale Mill Reach was developed as a residential area between 1888 and 1935. Because this area is highly urbanized, the geomorphic interpretation relies primarily on previous literature, historic aerial photography, and topographic maps.

Brook Village and Centredale Manor apartments now occupy the Centre Cotton Manufacturing Company Mill site. Floodplain deposits are mapped between the raceway of the former Centre Cotton Manufacturing Company Mill and the river channel. The mill and the subsequent apartment complexes were constructed on floodplain deposits. Although the site proved efficient in harnessing the waterpower for the mill, the floodplain is not desirable for urban development because of the high probability of flooding. The soil under the Brook Village and Centredale Manor development situated on the west and east banks of the Woonasquatucket River is classified as UD (Figure 8).

The MU soil unit dominates the east bank of the river. A river terrace is evident east of the apartment buildings. The kame terrace present at the

Greystone Mill site extends to the northern boundary of the river terrace (Figure 6).

West bank of the Woonasquatucket River

The valley train lies east of the two terraces and limits the movement of the river to the west. As a result, the position of the river on the west bank has changed very little since 1951 (Figure 7).

The MU soil unit also dominates the west bank of the river until Allendale Mill Pond. The soil of the west bank of the pond is classified as UD (Figure 8) and is the location of an asphalt company.

South Allendale Mill Reach

The South Allendale Mill Reach includes the Allendale Mill and extends south approximately 1,150 ft to the northern boundary of Lyman Mill Pond. The South Allendale Mill Reach illustrates the most complex geologic controls on migration of the Woonasquatucket River in the study site. The South Allendale Mill Reach is highly disturbed by anthropogenic influences.

East bank of the Woonasquatucket River

The Allendale Mill is situated on a river terrace, an ideal setting for the building because of the elevated topography of the terrace. Field investigations indicate that the river has been straightened at the point where water from the mill enters the river. During field investigations, an embankment parallel to the river was observed. The embankment consists of cobble-size rocks and is not continuous. Because of the discontinuous nature, the embankment does not always serve as a barrier between the river and the adjacent floodplain. The embankment is apparently the result of activity from dumping the spoils after the river was dredged because the cobble-size rocks found in the embankment are also found in the river channel bed. The height of the embankment varies, ranging from 1 to 4 ft from the river channel bed. Floodplain deposits were apparent to the west of this ridge and are indicative of overbank deposition.

A baseball field and recreational complex is located approximately 330 ft south of Allendale Mill. This area extends to the northern boundary of

Lyman Mill Pond and is classified as artificial fill in Figure 6. The soil overlain on the river terrace is the MU unit (Figure 8).

West bank of the Woonasquatucket River

Field mapping revealed two previous channels of the river, likely controlled by glacial outwash and influenced by the mill construction. In the 1888 United States Geological Survey 15-min topographic map, the river follows a sharp meander in response to glacial outwash but on the 1935 United States Geological Survey 7.5-min topographic map, the river abandons the meander loop and follows a straight path. This abandoned meander appears to be the response to a man-made cut-off where the river was straightened for the Allendale Mill raceway. The area within the meander, now classified as a wetland (State of Rhode Island Water Resources 2004), contains fine-grained sediment and organics deposited as the river adjusted to its new path and the meander was cut-off and filled. The soil in the meander is classified as Aa (Adrian muck) and supports the interpretation and observation of fine-grained and organic sediment found within the meander loop. A few erractics carried by glacial activity are present in the area of the meander.

A utility pole is located close to the abandoned meander and serves as additional evidence that this area has been disturbed. Aerial photographs in the 1960s reveal what appears to be a power line extending parallel with the river.

In 1981, aerial photography shows a wider river channel and lack of visible vegetation, indicating the acceptance of the wetland to overflow conditions of the river. As evident from the 1995 aerial photography, the most recent meander loop is still in communication with the river during time of high water.

The area north of the abandoned meander and south of the asphalt company is overlain by soil of the Pp (Podunk fine sandy loam) unit. This area is included with the floodplain deposits mapped on the west bank of the river and extends south of the north boundary of Lyman Mill Pond by approximately 660 ft.

A large percentage of the bed of Allendale Mill Pond is depositional, rather than erosional, and contains noncohesive sediment in much of the

channel. Based on aerial photography, sediment accumulation is not apparent on the east bank of the Allendale Mill Pond.

Lyman Mill Reach

Lyman Mill Pond exhibits a more quiescent environment than what is present in Allendale Mill Pond. A layer of organic muck 1 to 3 ft thick that occurs in most of the Lyman Mill Pond vibracores, which is described later in the section "Thickness of river channel deposits," prevents a continuous interpretation of the sedimentation record.

Two soil types dominate the Lyman Mill Reach; the MU (Merrimac-Urban land), which is more prominent on the east river bank, and the HkC (Hinckley gravelly sand loam, rolling), which exists only on the west river bank (Figure 8). From aerial photography and soil survey maps, the east bank of the river shows greater urban development than the west river bank thereby supporting the classification of an MU soil unit.

West bank of the Woonasquatucket River at Lyman Mill Pond

The MU soil unit borders the east bank of the river and continues to the cove that extends from the center of Lyman Mill Pond. This unit is also present west of the river at the southern limit of the pond. As verified in aerial photography, the MU soil complex on the east river bank represents a river terrace of the Woonasquatucket River. Field identification of this soil is difficult because of the intermingling of urban development with the Merrimac soil.

The UD (Udorthents-Urban land complex) soil borders the abandoned channel in the South Allendale Mill Reach and extends to the west bank of Lyman Mill Pond (Figure 8). The UD soil covers approximately 165 ft in the north section of the pond where it borders with the HkC soil. A Pg (pits, gravel) unit is located within the HkC soil and is the result of sand and gravel excavations. The sand and gravel are probable remnants of glacial deposits formed prior to the formation of the Woonasquatucket River. Two polygons of MU also exist within the HkC complex on the west river bank and south of the pond. Neither of the polygons is directly adjacent to the river.

The Ss (Sudbury sandy loam) soil unit, south of the gravel/sand quarry, is usually found in depressions on terraces and outwash plains. Directly

south of the pond is the Sb (Scarboro mucky sandy loam), a soil indicative of an area receiving an extensive amount of water. To the east of this unit, the Wa (Walpole sandy loam) is present. The sinuosity and location of the Wa soil appears to follow a path of historic river channel. The HkA (Hinckley gravelly sandy loam, 0 to 3 percent slope) forms adjacent to the eastern border of the Sb unit.

East bank of the Woonasquatucket River at Lyman Mill Pond

Similar to the Allendale Mill, the southern section of the Lyman Mill Reach includes a mill dam and pond. Along the east river bank, the soil is classified MU and, as expected, is highly urbanized (Figure 8). The MU soil covers much of the east river bank until the middle of Lyman Mill Pond. The Ss soil unit lies within the southern curve of the cove and extends south approximately 330 ft. The MmB (Merrimac sand loam) soil borders the eastern and southern boundaries of the Ss soil, terminating at the Lyman Mill Dam. This soil is usually found on terraces or outwash plains. As described by Smith (1956), this area is occupied by a river terrace of the Woonasquatucket River. Aerial photography supports the interpretation of a terrace based on a higher elevation than what is present on the west bank of the river and also by the presence of urban development (i.e., communities are more likely to build in areas not prone to flooding). The MmB soil was altered by the construction of Lyman Mill, an area mapped as a MU polygon adjacent to the southern extent the MmB soil (Figure 8).

A sand and gravel pit lies east of the MmB soil. This pit and the sand and gravel pit previously described on the west bank of the river at Lyman Mill Pond lie within the valley train.

Thickness of river channel deposits

Vibracores were used to map the thickness of river deposits for the Allendale and Lyman Mill Ponds. Isopach maps were constructed on individual horizons that were consistently present in the majority of the vibracores and are used to display the spatial extent of channel deposits.

In Allendale Mill Pond, the organic layer present along the bottom of the pond was measured and has the thickest accumulation of organics along the southern boundary (Figure 10). From the vibracores taken in Allendale Mill Pond, the mid-point of the pond exhibits the least amount of organic

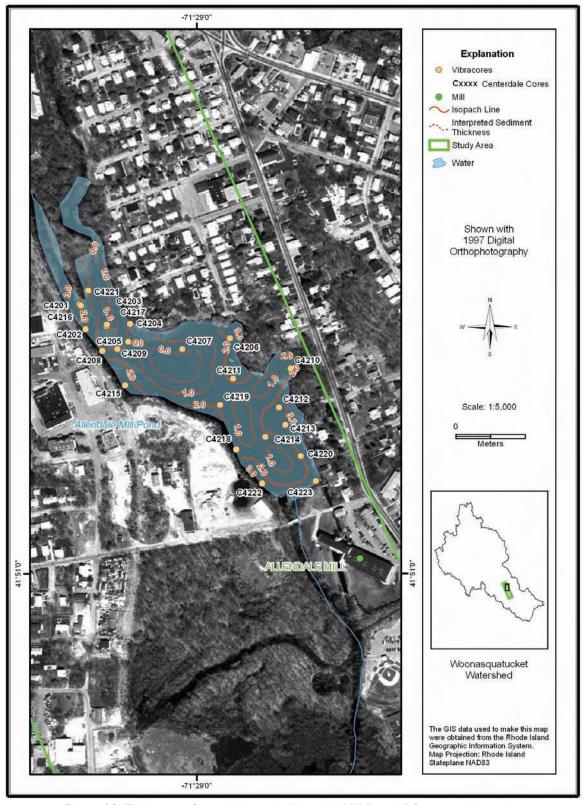


Figure 10. Thickness of organic layer in Allendale Mill Pond, 1-ft contour intervals.

deposition, an area where low flow occurs and where sediment was exposed during the 1991 Allendale Mill dam breach.

The organic muck layer, a field term used in describing the vibracores, is thought to be the result of sludge dumped into Lyman Mill Pond from the Lyman Mill in the early 1800s. Figure 11 is an isopach map of the measured thickness of the organic muck layer. The thickness of the organic muck ranges from less than 1 ft in the northern section of the pond to almost 4 ft in the southern portion. The vibracores were taken to a depth at which the coring device could no longer penetrate the sediment. Because of this, the vibracores may not have recovered the entire thickness of the organic muck layer at a particular vibracore location. The organic muck is present in all but one core, LPX-SD-4202, in the southern end of Lyman Pond. This area is situated on what is interpreted as a glacial ridge, a topographic high point of glacial debris.

A second layer, measured and mapped in the Lyman Mill Pond vibracores, consists of clay (Figure 12). The clay layer is below the organic muck. The clay layer shows the greatest accumulation in two locations, close to the dam where approximately 0.5 ft is present and in the northern neck of the pond opposite to the cove where approximately 1 ft has accumulated.

Streamflow analysis

A streamflow analysis and a review of watershed history and flood records can indicate changes in river morphology, which includes the landforms, but minor variation in the channel course. Changes, such as the abandoned channel in the South Allendale Mill Pond Reach, can be seen in aerial photography and topographic maps. River traces from aerial photography reveal minor changes in the channel course (Figure 7).

The effects of anthropogenic activities on the river regime are not always obvious using standard assessment methods, such as aerial photography and topographic maps, because of scale, resolution, or lack of data in the studied area. Flood events are an important aspect of geomorphic evolution and because of the random nature of floods and heavy rainfall, these events are studied as a probability problem. Guidelines for techniques used in the streamflow analysis can be found at Oregon State University (2005).

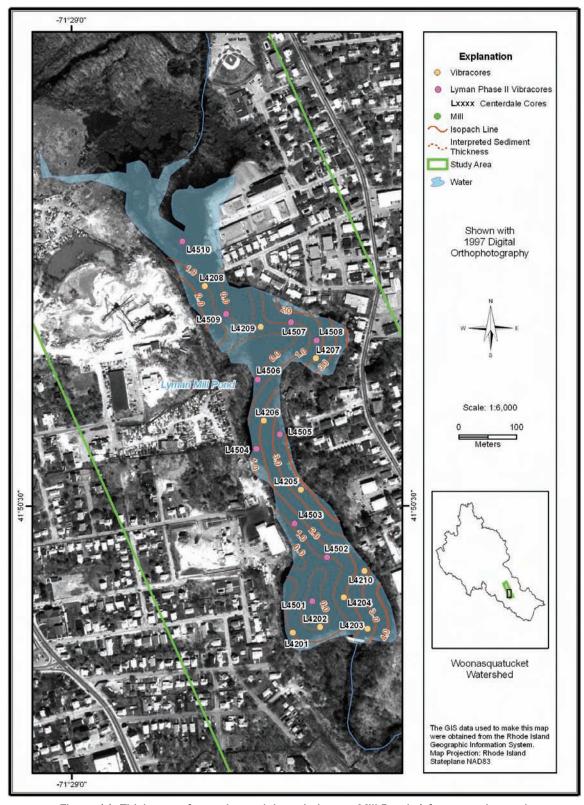


Figure 11. Thickness of organic muck layer in Lyman Mill Pond, 1-ft contour interval.

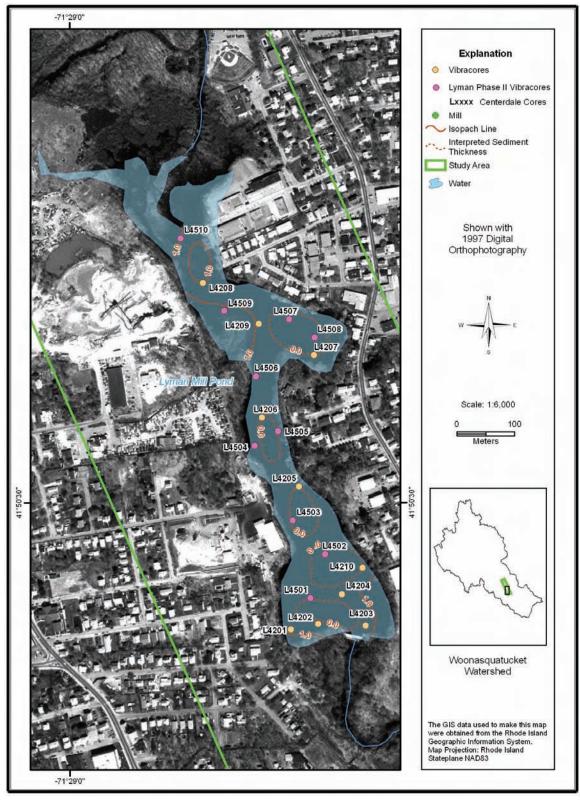


Figure 12. Thickness of clay layer in Lyman Mill Pond, 1-ft contour interval.

The Woonasquatucket River has one United States Geological Survey continuous real-time gage. The gage, United States Geological Survey 01114500, is located at lat 41° 51′ 32″, long 71° 29′ 16″, which is approximately 2,000 ft upstream of the Allendale Mill Dam (Figure 1) near Centerdale and approximately 95 ft NGVD 29 (National Geodetic Vertical Datum of 1929) above sea level. Real-time streamflow, peak streamflow, and daily streamflow are accessed via a Web site (United States Geological Survey 2005). Data not available at the Web site, such as historic gage height, were obtained directly from the United States Geological Survey.

In the study area of the Woonasquatucket River, mill ponds and dams were constructed prior to the implementation of the United States Geological Survey gage at Centerdale. The exception is the interval between the breach of Allendale Mill Dam in 1991 and the rebuilding of the structure in 2001.

The flow of the Woonasquatucket River is controlled primarily by regulation and quantities of reservoir and pond storage. By using the mean flow for the period of streamflow record and dividing by a drainage area of 38.2 square miles, the discharge per unit area for the Woonasquatucket River is 1.9 cfs/square mile.

According to the United States Department of the Interior (1982), flood events may occur as a result of a mixed population of precipitation events, such as rain with snowmelt and intense tropical storms with general cyclonic storms. For the most part, it is difficult to differentiate on the source of the flood events and the lasting impact of floods on the recorded streamflow. Because of this, flood events on the Woonasquatucket River are considered to be from one population.

Streamflow data for the Centerdale gage extend from 1943 to the present. Data extracted for this research include the water years 1942 to 2003. The mean annual streamflow is calculated by dividing the summation of daily streamflow by the days of recorded streamflow for that particular water year (WY). A water year includes the dates between October 1 of one calendar year to September 30 of the following calendar year to take into account the effect of seasonal variation in streamflow. The mean annual streamflow is derived and described and then ranked chronologically from highest to lowest value. This information identifies peaks within the data and is also used in analyses described later in this chapter.

Variation of mean annual flow

The mean annual flow is calculated for each water year and then compared to the overall mean flow for the period of 1942 to 2003. The plot of these data (Figure 13) allows visualization of the year-to-year variation of mean annual flows around the longer-term mean flow for the period of record and is also used to identify patterns of wet and dry years (Oregon State University 2005). Based on these calculations, data plotted for the Woon-asquatucket River reveal streamflow (Figure 13) that are linked to droughts and flood events in Rhode Island (Table 3). For example, the statewide drought during 1963 to 1967 is represented by significant below-average mean streamflow.

Mean monthly flow

The mean monthly flow as a ratio of annual flow is calculated from dividing the mean monthly flow by the mean annual flow for period of record and then multiplying by 100 to determine the percentage of annual flow (Oregon State University 2005). This calculation displays seasonal flow. Table 4 is the annual flow in the Woonasquatucket River that occurs for each month. The average monthly streamflow is highest in March with an average of 191.2 cfs and the lowest average monthly streamflow of 23.1 cfs occurring in September.

Moving mean

The moving mean is an average value calculated for a certain number of years and reduces the year-to year fluctuations and the extreme values in the period of record (Oregon State University 2005). For the Woonasquatucket River, the moving mean is calculated for 5-year and 11-year periods (Figure 14). An odd number of years is usually used when calculating the moving mean because data are plotted against the middle-most years (Oregon State University 2005). The 5-year and 11-year periods of record are selected because of the extensive streamflow record of 59 years so that enough wet and dry periods are within the moving mean calculations.

As evident from the 5-year moving mean in Figure 14, drought conditions prevailed in the middle- to late-1960s. The 11-year moving mean showed a smoother curve but displayed a definite decline in streamflow from 1952 to 1966.

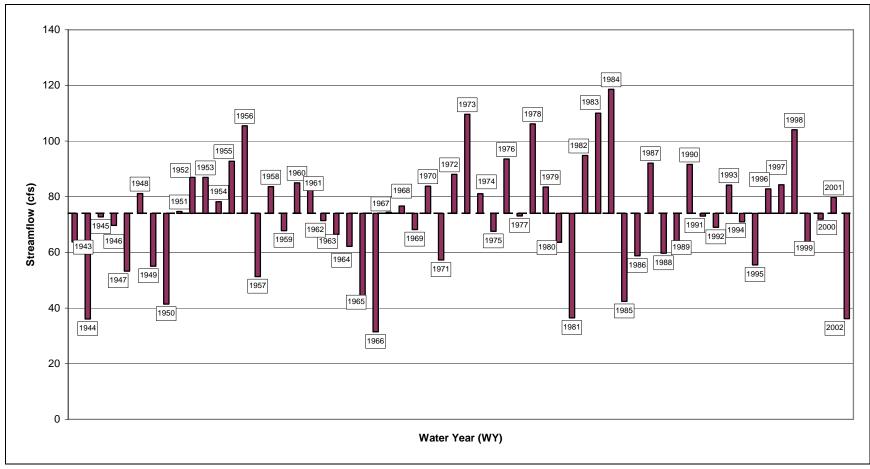


Figure 13. Variation of mean annual flow (74 cfs is the dashed horizontal axis) around longer-term mean flow from WY1943 to WY2003.

Table 3. Total precipitation and discharge for each water year with associated droughts, floods, and tropical systems.

Rank		Total Precipitation (Providence Gage) (in.)	Discharge (cfs)	Drought	Flood	Name of Tropical System	Date of Tropical System Impact	Category
1		40.6	1250					
2	1979	37.6	1160					
3	1987	35.9	1080			Chris	8/30/1988	Tropical Depression
4	1982	53.5	1030					
5	2001	31.8	986					
6	1983	62.6	979					
7	1956		870					
8	1998	40.3	831			Floyd	9/17/1999	Tropical Storm
9	1972	55.7	786					
10	1978	59.0	776					
11	1967	39.0	773		3/17-19/1968			
12	1969	49.9	754					
13	1970	42.3	700					
14	1976	43.7	694					
15	1984	39.4	682			Henri	9/24/1985	Tropical Storm
16	1973	44.9	586					
17	1993	47.0	568			Beryl	8/18/1994	Tropical Depression
						Carol	8/31/1954	Hurricane (Cat 2)
18		54.8	564			Edna	9/11/1954	Hurricane (Cat 2)
19		47.1	564					
20	1994	35.3	546					
21	1980	32.1	510	1980-1981 (Statewide)				
22		45.5	495	(Castomas)		Gordon	9/20/2000	Extratropical
-		39.7	494	1949-1950		Gordon	0,20,200	Exactopion
24		43.2	479					
		52.0	476					
26	1958		476					
	12000			1963-1967				
27	1962	48.2	469	(Statewide)				
28	1954	52.0	465			Diane	8/19/1955	Tropical Storm
00	1005	05.4	400	1963-1967			0.44.44000	
29	1965	35.4	438	(Statewide)	40 (00 (4000)	Alma	6/14/1966	Extratropical
30	1996	42.4	438		10/20/1996 to 10/21/1996	Josephine	10/9/1996	Extratropical
31	1974	43.7	413					
32	1957	56.8	411					
						Gracie	10/1/1959	Extratropical
33	1959		405			Brenda Donna	7/30/1960 9/12/1960	Tropical Storm Hurricane (Cat 2)
34		48.1	402			Bob	8/19/1991	Hurricane (Cat 2)
34	1990	40.1	402	1963-1967		BOD	8/ 19/ 1991	numcane (Cat 2)
35	1964	29.2	401	(Statewide)				
36	1961	40.0	392					
							6/31/1998	Thunderstorms
37		55.6	391				7/1/1998	Thunderstorms
38		47.0	383					
39		51.4	374			Able	9/2/1952	Tropical Depression
40		46.3	362					
41		52.1	357					
42	1960		340			Unnamed	9/15/1961	Tropical Storm
43		51.6	318					
44		55.0	296			Carrie	9/3-4/1972	Tropical Storm
45	1945		290					
46		49.0	285					
47		42.9	282					
48		38.7	259					
49		53.0	250		6/5-6/1982			
50	1947		249					
51	1946		249					
52	1943		244	1941-1945 (Statewide)		Great Atlantic Hurricane	9/14/1944	Hurricane (Cat 1)
53		44.5	243	(Ctatewide)		Halloween Storm	10/30/1991	Thunderstorm
54		46.5	207			Bertha	7/13/1996	Tropical Storm
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Rank		Total Precipitation (Providence Gage) (in.)	Discharge (cfs)	Drought	Flood		Date of Tropical System Impact	Category
55	1950	42.7	203					
56	1966	43.7	202	1963-1967 (Statewide)				
57	1944		195			Unnamed	10/21/1944	Extratropical
58	1985	40.1	164					
59	1949		154	1949-1950 (Statewide)		Dog	9/12/1950	Hurricane (Cat 1)

Table 4. Percentage of average monthly flow from WY1943 to WY2003 in the Woonasquatucket River. Values are in cubic feet per second.

Jan	Feb	Mar	April	May	June	July	August	Sept	Oct	Nov	Dec
124.0	137.6	191.2	176.5	117.0	80.9	42.8	38.9	23.1	52.1	81.5	116.8

Flood frequency analysis

There are several methods that are used for flood frequency analysis. The United States Department of the Interior (1982) recommends the Pearson Type III Distribution with log transformation (Log-Pearson Type III) using peakflow discharge as the basic distribution for defining the annual flood series. This procedure is also accepted by the United States Army Corps of Engineers and the United States Environmental Protection Agency and is, therefore, used in the flood frequency analysis of the Woonasquatucket River study site.

The Log-Pearson Type III distribution is derived using the following procedure:

- Organize data into water years.
- Calculate the mean, maximum, and minimum flows for each water year.
- Rank the discharge from largest to smallest streamflow for each water year.
- Calculate the log of each annual peak streamflow.
- Calculate the average peak Q and average of the log.

The procedure is applied by using the following general equation to derive flood magnitudes for various return periods (Oregon State University 2005):

$$\log x = \overline{\log x} + K\sigma_{\log x}$$

where:

x = the flood discharge value of some specified probability

log x = the average of the log x discharge values

K =frequency factor

 σ = the standard deviation of the log x values

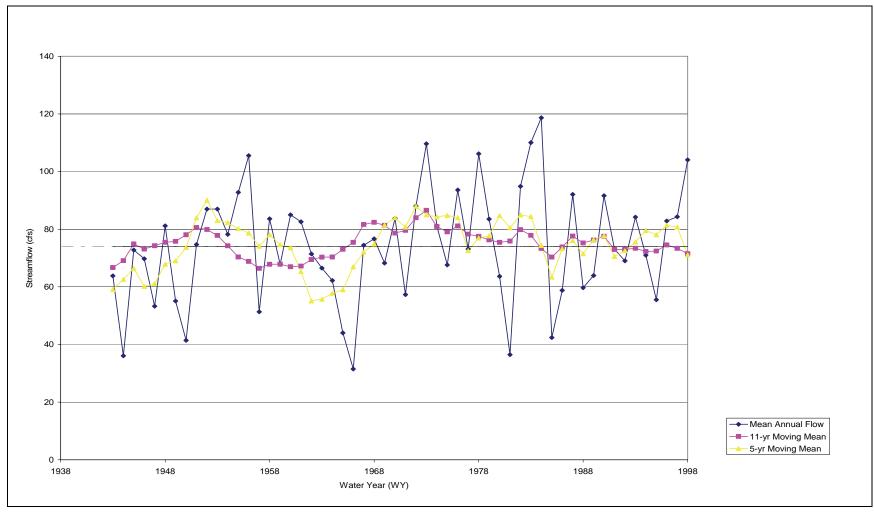


Figure 14. The moving mean indicating year-to-year fluctuations of the Woonasquatucket River for 5-year and 11-year periods (74 cfs is the dashed horizontal line).

According to Oregon State University (2005), the frequency factor K is a function of the skewness coefficient and return period and is found by using the frequency factor table.

Return intervals (Tr) are calculated using the equation:

$$Tr = [(n+1)/m]$$

where:

n = number of values in the dataset

m= the rank derived from the third step in the procedure of the Log-Pearson Type III distribution previously described.

The exceedence probability is then derived from taking the inverse of Tr(1/Tr).

The general equation addresses the magnitude of a specific discharge and the mean, variance, and standard deviation of the data can be calculated using the following formulas.

Variance =
$$\frac{\sum_{i}^{n} (\log Q - avg(\log Q))^{2}}{n-1}$$

Standard deviation =
$$\sigma log Q = \sqrt{variance}$$

After deriving the mean, variance, and standard deviation, the skewness coefficient, (Cs) is derived using the following equation (Oregon State University 2005):

Skew coefficient =
$$\frac{n x \sum_{i}^{n} (log Q - avg(log Q))^{3}}{(n-1)(n-2)(\sigma log Q)^{3}}$$

where:

n = the number of entries

x = the flood of a specified probability and $\sigma log x$ is the standard deviation

According to the Streamflow Research Project at Oregon State University, a K value is a constant that determines the asymmetry of the flood frequency diagram and is found using the frequency factor table.

Using equations previously described in this section, the flood frequency analysis for the Woonasquatucket River produces an estimated discharge and an associated return period. Figure 15 is a plot of the data displaying the frequency of the 2-year, 5-year, 10-year, 25-year, 50-year, 100-year, and 200-year floods.

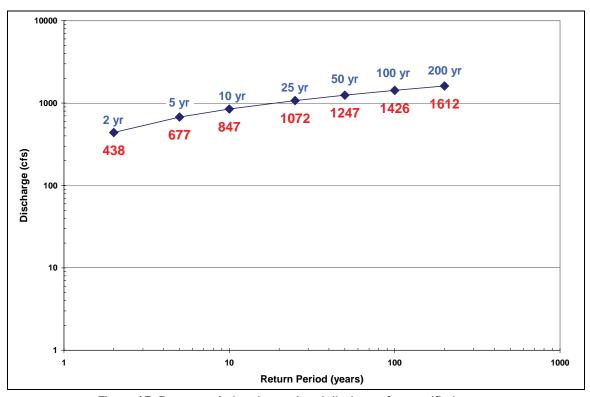


Figure 15. Return period and associated discharge for specified years.

As observed in the ranked peak discharge, eight of the 10 highest recorded flood events occurred since 1970, probably as a result of increased runoff from urbanization. Construction during urbanization leads to a decrease in groundcover, a decrease in infiltration, and, therefore, an increase in runoff.

4 Radionuclide geochronology

Introduction

Radionuclides, such as ²¹⁰Pb and ¹³⁷Cs, are used extensively for determining stratigraphic chronology in fluvial, lacustrine, and marine environments (Edington and Robbins 1976; Davis et al. 1984; Appleby and Oldfield 1992; and Appleby et al. 1995). The mill ponds of Allendale Mill and Lyman Mill lie within the fluvial environment of the Woonasquatucket River and mimic the environmentally closed system of a lake. The Greystone Mill site is on the floodplain of the Woonasquatucket River. The environmental and geographical location of the ponds support the use of radionuclide dating methods in reconstructing the history of sediment deposition in the river. This research applies ²¹⁰Pb and ¹³⁷Cs methods to the analysis of sediment at the Greystone Mill site and the Allendale Mill and Lyman Mill Ponds along the Woonasquatucket River in North Providence, RI.

Radiometric sediment age dating

In May 2003, 30 vibracores, 20 in Allendale Mill Pond and 10 in Lyman Mill Pond, were obtained to aid in interpreting the stratigraphic chronology of the Woonasquatucket River (Figure 6). Vibracores locations were chosen based on previous geomorphic analysis. The vibracores, averaging 4 ft in length, were slabbed, described, and subsampled for radioisotope analyses. Subsamples were extracted from the core every 0.8 in., but not all were analyzed for radionuclides. Twenty-one pushcores were taken at the Greystone Mill site, on the floodplain of the Woonasquatucket River in what is believed to have been the raceway of the former powder mill.

Cultural debris (plastic bag) was recovered in core CMS-SD-4221 eliminating this core as a possible dating point. Only one vibracore in Lyman Mill Pond, LPX-SD-4201, recovered sediment that could be used in the ²¹⁰Pb and ¹³⁷Cs analyses. The core recovery at Lyman Mill Pond was excellent but because of the presence of unconsolidated organic muck, the sediment recovered did not support ²¹⁰Pb and ¹³⁷Cs analyses. In May 2005, Phase II of Lyman Mill Pond sampling was conducted to recover sediment suitable for ²¹⁰Pb and ¹³⁷Cs analyses. Sampling followed the same technique used in the May 2003 campaign with one exception. Vibracores were allowed to

drain for several days in a refrigerated cooler prior to extracting samples for radioisotope dating.

Sediment age dating using ²¹⁰Pb

Principles of ²¹⁰Pb sediment age dating

In the ²³⁸U decay series, the radium isotope ²²⁶Ra, with a half-life of 1,622-year decays to the inert gas ²²²Rn (radon), which then decays through four short-lived isotopes, each measured in a half-life of minutes, to ²¹⁰Pb (Applebyand Oldfield 1983). The half-life of ²¹⁰Pb is 22.3 years (Appleby 2001). Radon, with a half-life of 3.83 days (Nozaki et al. 1978), is present in varying amounts in sediments and diffuses from the earth's crust into the atmosphere. As radon is isolated from its precursor by changing phases from solid to gas, the initial secular equilibrium is destroyed. A new secular equilibrium is reached as the isotope ²¹⁰Pb becomes the predominant radionuclide.

To become airborne, ²¹⁰Pb attaches to aerosols in the atmosphere, which are then deposited on the earth's surface by dry fallout or precipitation. The existence of ²¹⁰Pb in the atmosphere is short-lived, with a mean atmospheric residence time of the order of 5 to 10 days (Krishnaswami and Lai 1978). Therefore, deposition takes place on a time scale much shorter than the half-life of the isotope (Gale et al. 1995).

The total ²¹⁰Pb inventory is divided into a supported component from the ²²²Rn decay within the sediment column, and an unsupported or excess component from atmospheric fallout of the ²¹⁰Pb radioisotope (Appleby and Oldfield 1983). The unsupported ²¹⁰Pb activity is the component of the total ²¹⁰Pb inventory that declines with age in accordance with the usual radioactive decay law (Appleby and Oldfield 1983).

Unsupported or excess ²¹⁰Pb is that ²¹⁰Pb produced from atmospheric fallout when it is no longer in equilibrium with its parent ²²⁶Ra. The supported ²¹⁰Pb is produced in situ from the decay of ²²²Rn in lithogenic material and is in equilibrium with that of the parent, ²²⁶Ra. After ²¹⁰Pb is incorporated into the soil, it decays exponentially with time in relation to its half-life. The exponential decay of unsupported ²¹⁰Pb is determined by the decay constant of the ²¹⁰Pb nuclide and thereby provides a useful dating method if the initial activity is known. Thus, the age or accumulation

rate of a deposit can be determined by a general decay equation of the form (Ivanovich and Murray 1992):

$$C = C_0 e^{-\lambda t}$$

where:

$$C_0=$$
 initial ²¹⁰Pb activity
$$\lambda=ln\frac{2}{22.26}y\cong 0.03114\ y^1, \ \text{the radioactive decay constant}.$$

The age, t, is calculated if the initial 210 Pb activity can be derived from a suitable model (Appleby and Oldfield 1992).

Radioactive decay is a random process that follows a Poisson distribution wherein the true variance of a Poisson variable equals its true mean (Binford 1990), therefore, the square root of the mean provides an estimate of the standard deviation.

The isotope ²¹⁰Pb enters the fluvial environment by two mechanisms, runoff with subsequent deposition of suspended sediment, and atmospheric fallout, usually from precipitation. The amount of ²¹⁰Pb that enters a water body is influenced by biogeochemical and hydrological characteristics of the watershed (Binford 1990). Because ²¹⁰Pb is quickly sorbed to finegrained sediments and organics, it is rapidly incorporated into the sediment column where little mobilization occurs (Binford 1990). The unsupported ²¹⁰Pb activity offers the potential for estimating sedimentation accumulation rates but the difficulty is in isolating the components of the total inventory.

Previous research

Numerous publications document the use of ²¹⁰Pb as a tool for reconstructing geochronology in sediments deposited during the last 150 years. Goldberg (1963) introduced the use of naturally occurring ²¹⁰Pb in sediment dating through its application to glacier cores. Krishnaswami et al. (1971) applied the same reasoning to the sedimentation process in lakes with the added assumption that the residence time of ²¹⁰Pb in the water column is short enough that the input flux reaches the lake bottom

attached to sedimentary particulates without any dispersion (Durham and Joshi 1980).

Appleby and Oldfield (1983) further advanced the use of ²¹⁰Pb as a dating tool by introducing the concept that varying sediment accumulation rates affect the initial ²¹⁰Pb concentration. They determined that the Constant Rate of Supply (CRS) model provides a reasonably accurate chronology when the total ²¹⁰Pb contents of cores from neighboring locations are comparable.

Other researchers (Dukat and Kuehl 1995) observed that downcore ²¹⁰Pb cyclicity is affected by the sampling scheme used. Dukat and Kuehl (1995) also noted that samples collected at 0.8-in. intervals throughout the length of cores give optimal representation of the nature and frequency of the ²¹⁰Pb cyclicity in their study site in the Amazon continental shelf. Although other researchers found that a relationship exists between ²¹⁰Pb activities, grain-size, organic carbon, or clay-sized mineralogy, Dukat and Kuehl (1995) reported that such a relationship does not exist in their study region.

Farmer (1978) studied the effects of sediment compaction on sedimentation rates and applied a depth correction by normalizing wet-dry ratios (on a volume basis) in uncompacted sediments to that of fairly constant wet-dry ratios at depth. In a study of Lake Ontario, Farmer (1978) discovered that allowance for compaction reduces the noncompaction-corrected sedimentation rates by 20 to 30 percent.

Binford (1990) conducted an uncertainty analysis using first-order error analysis and Monte Carlo simulation of ²¹⁰Pb dates. The purpose of his study was to assess sources of errors in ²¹⁰Pb models used for the Florida Paleoecological Investigations of Recent Lake Acidification (PIRLA) project. He concluded that first-order error analysis proved sufficient for cores at dates less than 130 years calculated from the Constant Rate of Supply (CRS) model used in the study. The first-order error analysis is not valid for other models.

Appleby (2000) found that the ²¹⁰Pb dating technique is not always applicable in remote mountain lakes. Because of episodic changes, sedimentation accumulation rates and ²¹⁰Pb supply rates were not in proportion in some cores taken in these lakes so neither the CRS nor the Constant Initial

Concentration (CIC) models were valid. Instead, Appleby (2000) relied on ¹³⁷Cs and ²⁴¹Am (americium), another artificial radioisotope derived from fallout of nuclear weapons, to construct a reliable core chronology.

Laboratory analytical procedures

The radiological laboratory, Teledyne Brown Engineering, Incorporated, commonly known as Teledyne, located in Knoxville, TN, conducted the ²¹⁰Pb and ¹³⁷Cs laboratory analyses used in this study. Teledyne Brown Engineering, Incorporated, is a business segment of Teledyne Technologies that supports government and commercial endeavors in the engineering and scientific fields.

Because ²¹⁰Pb emits a low energy beta particle, it is difficult to measure directly so the daughter, ²¹⁰Bi or the granddaughter ²¹⁰Po emission is analyzed. Teledyne measures ²¹⁰Bi through its emission of a beta particle to calculate the ²¹⁰Pb activity. The sample is leached with hot hydrochloric acid to extract the ²¹⁰Bi and assay its beta activity. Lead is diluted first with 9M hydrochloric acid and deionized water and bismuth is then eluted with 2M sulphuric acid and precipitated as the oxychloride (Teledyne 2001). According to the laboratory procedure described by Teledyne (2001), the ²¹⁰Bi is collected by vacuum filtration on a 1-in. glass fiber disc and the bismuth yield is gravimetrically determined. The filter disc is mounted on a nylon planchet and covered with 3 mg/cm² aluminum absorber for beta assay in a low-level, gas-flow proportional counter.

Detection capability depends upon sample size, chemical yields during processing, counting time, and the efficiency and background of the counting instrument (Teledyne 2001). According to the laboratory procedure outlined by Teledyne (2001), with a sample weight of 10 g (dry), a chemical yield of 0.5, and a counting interval of 100 min, the minimum detectable activity (MDA) for leachable 210 Pb in soils and sediments is nominally 0.2 picocuries per gram (piC/g) at the 4.66 sigma level using a counter background of 0.3 counts per minute (cpm) and an efficiency of 0.23 for 210 Bi counting. A representative decay factor of 0.9 allows for 1-day delay in counting the planchet after lead separation (Teledyne 2001).

The equation used for calculating activity and the 2σ counting error is:

$$\frac{Net \ pCi \ on \ counting \ date}{gram} = \frac{(N/\Delta t - \beta)}{2.22(\nu)(y)(DF)(\epsilon)} \pm \frac{2\sqrt{(N/\Delta t - \beta)}/\Delta t}{2.22(\nu)(y)(DF)(\epsilon)}$$
net activity counting error

where:

N =total counts from sample (counts)

 $\Delta t = \text{counting time for sample (min)}$

 β = background rate of counter (cpm)

2.22 = dpm/pCi

v = weight of sample analyzed (g)

y = chemical yield of the mount or sample counted

DF =decay factor of ²¹⁰Bi from the mid-elution time to the midcount time

 ϵ = efficiency of the counter for ²¹⁰Bi beta counting, using a No. 1 (3 mg/cm²) absorber.

Because the total inventory of ²¹⁰Pb is reported in the laboratory analysis, it is necessary to separate the unsupported ²¹⁰Pb from the total ²¹⁰Pb, so that:

$$^{\rm 210} Pb_{\rm UNSUPPORTED} = ^{\rm 210} Pb_{\rm TOTAL} - ^{\rm 210} Pb_{\rm SUPPORTED}$$

The first step in calculating ²¹⁰Pb_{UNSUPPORTED} is to plot the reported ²¹⁰Pb_{TOTAL} activity in relation to the sample depth. The ease with which vertical profiles of unsupported ²¹⁰Pb in the sediment column can be interpreted, and hence the ease with which sedimentation accumulation rates can be determined, is dependent on several factors including possible historical changes in sedimentation accumulation rates, degree of compaction of the sediment and extent of post-depositional mobility, if any, of ²¹⁰Pb in the sediment column through mixing or redistribution due to biological activity, diffusion or slumping (Farmer 1978).

Using this vertical depth profile, the ²¹⁰Pb activity is then separated into three regions; sediment mixing, radioactive decay, and background (supported) ²¹⁰Pb as described by Bierman et al. (1998). Background ²¹⁰Pb is assumed when the ²¹⁰Pb decays to a constant activity and is in equilibrium with the in situ ²²⁶Ra. These values are averaged and then subtracted from each sampling depth to yield the unsupported component of ²¹⁰Pb. However, it is important to note that the overall decrease in ²¹⁰Pb activity might

give an indication of in situ decay and therefore age, but the variability from sample to sample is considerable (Bierman et al. 1998) because of the rarity of the entire sampling environment meeting all assumptions required of calculating ²¹⁰Pb chronology.

Chronology models for ²¹⁰Pb

Introduction

Several models for ²¹⁰Pb analysis have been developed using the radioactive decay equation. Model selection depends on environmental conditions, geologic processes (i.e., erosion, deposition), sediment focusing, and sediment stability. In this research, the Constant Flux:Constant Sedimentation (CF:CS), Constant Rate of Supply (CRS), and Constant Initial Concentration (CIC) models are used to calculate sediment age at sample depth. The main distinction between the latter two is that the CRS assumes a constant atmospheric flux of ²¹⁰Pb and the CIC is governed by a varying sedimentation accumulation rate that does not affect the ²¹⁰Pb concentration. If a ²¹⁰Pb activity-to-depth profile is nonlinear and strongly nonmonotonic then only the CRS model offers a method to interpret the stratigraphic chronology.

The limitations of these models are due primarily to selecting the background level of ²¹⁰Pb and the number of samples analyzed. Based on assumptions inherent with any sediment dating models, the derived dates can only be considered as estimates.

In accordance with the radioactive decay equation, the exponential decay of ²¹⁰Pb should display a linear, monotonic profile (Appleby and Oldfield 1983; Abril 2004). However, other researchers have observed nonmonotonic and nonlinear ²¹⁰Pb activity profiles produced from depositional and erosional cycles (Appleby and Oldfield 1983). The problem arises when the same ²¹⁰Pb data produce different results calculated from different models (Abril 2004). Because of this, it is necessary to validate the ²¹⁰Pb geochronology with a time-dependent marker. In this research, ¹³⁷Cs is plotted with ²¹⁰Pb model dates to produce a more effective model of age estimation. Although corrected CRS model dates can be calculated using the 1963 ¹³⁷Cs date as a reference point, errors can still arise due to variations in the ²¹⁰Pb supply rate at individual core sites from local irregularities in the process of sedimentation (Appleby 2000).

As with all models, there are certain assumptions that are incorporated into the calculations. Each model contains its own assumptions that are mentioned in the following sections but those that are basic to all models of the ²¹⁰Pb method include the following (Noller 2000):

- ²¹⁰Pb is quickly removed from the atmosphere and freshwater streams and sequestered in soils and sediments.
- 210Pb is immobile once deposited.
- Unsupported ²¹⁰Pb does not migrate down into the sedimentary column.
- Supported ²¹⁰Pb is in secular equilibrium with its grandparent ²²⁶Ra.
- Unsupported ²¹⁰Pb is independent of depth.

Fluvial systems are dynamic, with erosion and deposition varying in a single geomorphic regime. In bodies of water that reflect varying sedimentation accumulation rates, unsupported ²¹⁰Pb activity will vary with depth and display a nonlinear profile. According to Appleby (2001), nonlinearities in the ²¹⁰Pb record may be due to a number of different processes, such as:

- Dilution of the atmospheric fallout by increased sedimentation rates.
- Varying degrees of sediment focusing.
- Interruptions to the normal process of sediment accumulation.
- Mixing by physical, biological, or chemical processes.

The CRS model is usually appropriate in bodies of water where there has been little or no sediment disturbance. Sediment mixing typically results in a flattening of the profile of ²¹⁰Pb activity versus depth in the surficial sediment layers, and degradation of the ¹³⁷Cs peak (Appleby 2001).

In Allendale Mill Pond, the most recent probable impact on the sediment regime is the 1991 dam breach. However, it is uncertain how much the dam breach affected ²¹⁰Pb distribution in the stratigraphic record. Taking this into consideration, it is possible that the CIC model would yield better results, assuming that the dam breach did not alter the initial ²¹⁰Pb concentration record. However, Appleby (2001) observes that discrepancies with the CIC model date indicate variations in the initial ²¹⁰Pb concentration and can be due to a variety of causes, such as flood events, sediment slumps, turbidity events, and major land-use changes. Although the 1991 dam breach disturbed the sediment regime, it may not have significantly

impacted the stratigraphic record or altered the ²¹⁰Pb concentration. In any event, to determine model suitability, the best procedure is to interpret the ²¹⁰Pb laboratory data using the CIC and CRS models in addition to the CF:CS model.

Sedimentation rates are calculated from the CF:CS, CRS, and CIC models previously described. Sediment ages are then derived from each model by using the appropriate equation for each model and the sampling date for Lyman Mill and Allendale Mill Ponds. In order to ascertain model equality of the sediment ages produced from the CF:CS, CRS, and CIC models, a statistical test for multiple comparisons, the Kruskal-Wallis Rank test, also known as the H-distribution, is applied to test the null hypothesis of model equality.

Constant flux and constant sedimentation rate (CF:CS)

Mass sediment accumulation rates are a measure of sedimentation where there are changes with depth in sediment density that relate to compaction or changes in sediment composition. These sedimentation rates are determined by plotting the log of the excess ^{210}Pb activities against cumulative dry sediment weights and calculating sedimentation rates over intervals of constant slope (Brush et al. 1982). The sedimentation rate can be calculated using the slope of the line derived from the linear regression of $\ln^{210}\text{Pb}_{\text{UNSUPPORTED}}$ and sample depth in the following equation (Bierman et al. 1998):

$$A(z) = A(o)e^{-bz}$$

The rate of sedimentation, S, is equal to λ/b in cm/year, where

 $\lambda = {}^{210}Pb$ radioactive decay constant of 0.03114

A(z) =excess ²¹⁰Pb activity at depth z

A(o) = activity at the surface (or bottom of the uniformly mixed layer)

b = the slope defined by a regression through the data

z =depth.

Assuming a constant activity at the surface, the model is simplified to the following equation:

$$S = \frac{\lambda_{210_{Pb}}}{b}$$

where the slope (b) of the regression line through data is plotted as the natural log of unsupported ²¹⁰Pb activity as a function of sample depth.

Constant initial concentration (CIC)

The CIC model, also known as constant specific activity model, assumes that an increased flux of sedimentary particles from the water column will remove proportionally increased amounts of ²¹⁰Pb from the water to the sediments (Appleby et al. 1983) and will increase or decrease in response to changes in sedimentation. The CIC model assumes that the vertical sediment accumulation rate will not affect the ²¹⁰Pb concentration and that it will remain constant. If the initial concentration in the sediment is low then the unsupported ²¹⁰Pb will require less time to decay to a level indistinguishable from the supported ²¹⁰Pb than if it was initially high (Pennington 1976).

The unsupported ²¹⁰Pb concentration will vary with depth in accordance with the formula (Appleby et al. 1983):

$$C = C(o)e^{-\lambda t}$$

where C(o) is the unsupported ²¹⁰Pb concentration of sediments at the sediment water interface and the radioactive decay constant (λ) of ²¹⁰Pb is:

$$\lambda_{210_{p_b}} = \frac{\log 2}{22.26} = 0.3114y^{-1}$$
 or $\lambda_{210_{p_b}} = \ln \frac{2}{22.26y} = 0.03114y^{-1}$, as

previously stated.

According to Appleby and Oldfield (1983), the age of sediment layers with ²¹⁰Pb concentration *C* is therefore:

$$t = \frac{1}{\lambda_{210_{Pb}}} ln \frac{C(o)}{C}$$

Constant rate of supply (CRS)

Based on the law of radioactive decay, Krishnaswamy and Lai (1971) developed the CRS model, also referred to as the Constant Flux model, to

determine the age of a given depth within a sediment column. The CRS model is the most widely accepted model and is dominated by a constant direct atmospheric fallout (Appleby et al. 1990). Other assumptions inherent in the model include that the initial ²¹⁰Pb concentration in the sediment is variable, the influx rate of sediment is variable, (Noller 2000) and that no post-depositional mixing occurs. Another assumption is that the transport parameters are independent of sedimentation rate. However, although corrected CRS model dates can be calculated using the 1963 ¹³⁷Cs date as a reference point, errors can still arise due to variations in the ²¹⁰Pb supply rate at individual core sites from the local irregularities in the process of sedimentation (Appleby 2000).

According to Appleby and Oldfield (1978), the initial concentration Co(t) of unsupported ²¹⁰Pb in sediment of age t years must satisfy the following:

$$C_0(t) r(t) = constant$$

where r(t) (g/cm² year) is the dry mass sedimentation rate at time t.

From this equation, Appleby and Oldfield (1978) developed a relation for the age of deposit at depth x:

$$t = \frac{1}{\lambda} ln \left(\frac{A_0}{A_r} \right)$$

where A_o is the total unsupported ²¹⁰Pb activity in the sediment column and A_x is the total unsupported ²¹⁰Pb activity in the sediment column beneath depth x (Noller 2000).

The sedimentation rate, r, is calculated directly from the formula (Appleby and Oldfield 1978):

$$r = \frac{\lambda A_x}{C}$$

The net flux of ²¹⁰Pb to sediments is calculated by the following equation (Binford et al. 1993):

$$P = \sum^{210} Pb_{UNSUPPORTED^{\lambda}}$$

where $\sum^{210} Pb_{UNSUPPORTED}$ is the sum of the unsupported activity and P is the net flux. The result should not exceed the global 210 Pb natural atmospheric flux of 1.3 to 5.8 pCi in-2 y-1 (Appleby and Oldfield 1983) providing an indication of validity of 210 Pb observations. None of the samples used in 210 Pb analysis taken from the vibracores in Allendale Mill Pond exceed the 210 Pb natural atmospheric flux. The average 210 Pb net flux for the vibracores is 2.58 pCi in-2 y-1.

Statistical analysis

Introduction

The greatest source of uncertainty in interpreting ²¹⁰Pb activity is in identifying the zone of supported ²¹⁰Pb. As the excess ²¹⁰Pb activity approaches the value of the background-supported activity, the uncertainty of individual activity measurements becomes larger (Brush 1982). Errors may also arise in the zone of supported ²¹⁰Pb if the ²¹⁰Pb activity from the cores does not extend to a determinable background level. If the supported ²¹⁰Pb activities are indeed higher than what actually exists then calculated sediment accumulation rates are generally higher than the actual accumulation rates.

Binford (1990) observes that the standard error of the mean for one observation from a known distribution is equal to the standard deviation. He explained that the supported ²¹⁰Pb is estimated by calculating the mean and standard deviation of the bottom three determinations of ²¹⁰Pb in the lower section of the core. If the next higher activity in the core is less than the mean plus one standard deviation, the mean and standard deviation are recalculated with the new level included (Binford 1990). This process continues moving from deep to shallow sample depths until the activity in the next sample depth is greater than the mean plus one standard deviation. The level reached reflects the lowest interval with measurable, unsupported ²¹⁰Pb and is the interval included in the regression analysis. The standard deviation of supported ²¹⁰Pb is incorporated into the standard deviation of unsupported ²¹⁰Pb by the simple relation (Binford 1990):

$$S_{\mathit{UNSUPPORTED}} = \left(S^2_{\mathit{SUPPORTED}} + S^2_{\mathit{TOTAL}}\right)^{0.5}$$

where $S_{SUPPORTED}$ is the standard deviation of unsupported $^{210}{\rm Pb}$, $S^2_{SUPPORTED}$ is the calculated variance of supported $^{210}{\rm Pb}$, S^2_{TOTAL} is the

variance of total ²¹⁰Pb activity in an analyzed interval (counting error). This method of standard deviation is used in this research as well as calculating the supported ²¹⁰Pb by vertical depth profiles when the ²¹⁰Pb activity is plotted against depth. The difference between the vertical depth profiles and the standard deviation is negligible in the vibracores used in this research.

In the regression analysis, the linear regression is based on the principle of least squares. The least squares method is a goodness-of-fit line that summarizes the variables and produces a mathematical model of the data. The least squares line has the property that the sum of the squared vertical distances from it to points on the scatter diagram is smaller than the similar sum for any other line (Dunn and Clark 1987). In this research, the least squares method is applied by using a scatter plot function in the Microsoft Excel 2000 software program. The data plotted are the natural log of the unsupported ²¹⁰Pb (y-axis) as a function of depth (x-axis).

The correlation coefficient (r) produces a value between -1 and +1, where -1 suggests a prominent negative relationship and 1 is a strong positive relationship. The relative magnitude of a correlation coefficient (r) is not proportional, making it difficult to use in comparisons with other correlation coefficients (r). In order to better interpret the linear relationship of the variables, the coefficient of determination (r^2) is used. The coefficient of determination (r^2) is the squared value of r and is derived from the following equation (Devore and Farnum 1999):

$$r^2 = 1 - \frac{SS Re sid}{SSTo}$$

where SSResid is the amount of variation in y that cannot be attributed to the linear relationship between x and y and SSTo is a measure of total variance. The coefficient of determination represents the variation in x in association with the proportion of y. In using the coefficient of determination with the 210 Pb models, the year calculated from the individual model is plotted versus the sample depth. Each model is plotted separately for each vibracore. A linear regression is performed to calculate the coefficient of determination (r^2) so that the variation in the year (age of sediment at a specific sample depth) with respect to the sample depth is revealed. Table 5 is a list of the Allendale Mill Pond vibracores with the calculated coefficient of determination (r^2) . All of the vibracores yielded r^2 values of

greater than 50 percent, with the exception of CMS-SD-4210 and CMS-SD-4222.

Vibracore	Correlation Coefficient (r)	Coefficient of Determination (r ²)
CMS-SD-4204	0.97	0.95
CMS-SD-4206	0.99	0.99
CMS-SD-4209	0.98	0.97
CMS-SD-4210	0.35	0.12
CMS-SD-4212	0.90	0.82
CMS-SD-4213	0.87	0.75
CMS-SD-4218	0.82	0.67
CMS-SD-4222	0.69	0.48

Table 5. Coefficient of determination (r^2) for Allendale Mill Pond vibracores.

Kruskal-Wallis rank test

The Kruskal-Wallis Rank test is the nonparametric analogy to the parametric one-way analysis of variance (ANOVA) test and is an extension of the Mann-Whitney test, used when three or more data sets are compared. The Kruskal-Wallis Rank statistic assumes that populations are continuous and of the same distribution. Data are ranked and the median is used to test the null hypothesis that population means are equal. As is typical with nonparametric tests, the Kruskal-Wallis test does not require equal sample sizes and is applicable to small sample populations.

In this research, the Kruskal-Wallis Rank test is used to test the null hypothesis for the sediment ages derived from the models in the 210 Pb analysis, such that CF:CS Model = CIC Model = CRS Model. The alternative hypothesis is that the models are not equal. All observations are ranked from 1 to n_{TOTAL} and the following test statistic is used (Neter and Wasserman 1974):

$$K = \frac{\sum_{j=1}^{r} n_{j} \left(\overline{R}_{\cdot,j} - \overline{R}_{\cdot,j}\right)^{2}}{\frac{n_{T}(n_{T}+1)}{12}}$$

The numerator is the usual treatment sum of squares but with data expressed in ranks, the denominator is the variance of the ranks 1, 2,

3,..... n_{TOTAL} , and the test statistic K can be expressed equivalently as follows (Neter and Wasserman 1974):

$$K = \frac{12}{n_T(n_T + 1)} \sum_{j=1}^{r} n_j \overline{R}^2{}_j - 3(n_T + 1)$$

According to Neter and Wasserman (1974), if the n_j is reasonably large (5 or more), K is an approximate χ^2 random variable with r-1 degrees of freedom when C_1 (all models are equal) holds. The null hypothesis, C_1 , is stated as:

and the alternative hypothesis, C_2 concludes that not all models are equal.

If the null hypothesis is not accepted, it is important to note that the test cannot make the distinction as to which models are not equal. For the null hypothesis to be accepted, the three models must all share equal medians.

The Kruskal-Wallis H-statistic is calculated and an approximate probability value (p-value) is derived. A large p-value supports the interpretation that the models yield similar sediment ages, while a small p-value supports (for example, less than 0.05) the interpretation that it is appropriate to reject the hypothesis that the estimates of sediment ages are similar.

The H-statistic is a close approximation of the chi square (χ^2) distribution with k-1 degrees of freedom if the null hypothesis of equal populations is true. Because of this, the chi-square (χ^2) is used to determine acceptance or rejection of the null hypothesis. Using the p-value associated with the observed χ^2 , a value is selected from a statistics table to determine if the null hypothesis is accepted. If the Kruskal-Wallis H-statistic is less than χ^2 , then the null hypothesis is accepted. Based on these criteria, the null hypothesis that all models are equal is accepted for all vibracores except CMS-SD-4212. The three models are not equal for CMS-SD-4212 and the null hypothesis is rejected. Table 6 shows the Kruskal-Wallis H-statistic, χ^2 , and the p-value for the Allendale Mill Pond vibracores.

Confidence interval

CMS-SD-4222

2.56

A confidence interval (CI) of 95 percent was applied to the three models used to calculate the year of deposition by assessing the ²¹⁰Pb activity

Kruskal-Wallis Probability **Null Hypothesis** Accepted Vibracore Statistic χ2 (p) CMS-SD-4204 5.99 5.59 0.0611 Yes CMS-SD-4206 4.06 5.99 0.1313 Yes CMS-SD-4209 4.02 5.99 0.1339 Yes CMS-SD-4210 5.97 5.99 0.0504 Yes CMS-SD-4212 8.76 5.99 0.0126 No CMS-SD-4213 3.42 5.99 0.1806 Yes CMS-SD-4218 4.68 5.99 0.0965 Yes CMS-SD-4219 0.22 5.99 0.8968 Yes

Table 6. The Kruskal-Wallis H-statistic, $\chi 2$, and the ρ -value for the Allendale Mill Pond vibracores.

results from two vibracores, CMS-SD-4204 and CMS-SD-4206 (Table 7). The dates calculated from each model were entered into SigmaPlot 8.0 and the CI boundaries were derived from the plots.

5.99

0.2778

Yes

With the exception of the year calculated for the lowest sample depth in both cores using the CRS model, the years from each of the models fell within the 95 percent confidence interval (Figure 16 and Figure 17). The point that is outside the 95 percent CI is at a depth of approximately 5 in., indicating that the CRS model is applicable in depths less than 5 in. when calculating sediment age.

With the exception of the year calculated for the lowest sample depth in both cores using the CRS model, the years from each of the models fell within the 95 percent confidence interval (Figure 16). The point that is outside the 95 percent CI is at approximately at a depth of 5 in., indicating that the CRS model is applicable in depths less than 5 in. when calculating sediment age.

Table 7. Data for vibracores CMS-SD-4204 and CMS-SD-4206 used in assessing confidence interval.

Sample Interval	CF:CS (Year)	CIC (Year)	CRS (Year)
Vibracore CMS-SD-4204			
0.025	1999	2003	1993
0.125	1983	1992	1988
0.225	1967	1957	1977
0.325	1951		
0.425	1935		
0.525	1919	1925	1959
0.725	1887		
0.925	1855		
1.025	1839		
Vibracore CMS-SD-4204			
0.050	1998	2003	1996
0.325	1973	1975	1984
0.525	1955	1960	1977
0.725	1936		
0.925	1918		
1.525	1863		
1.175	1895		
1.375	1876		
2.225	1798		

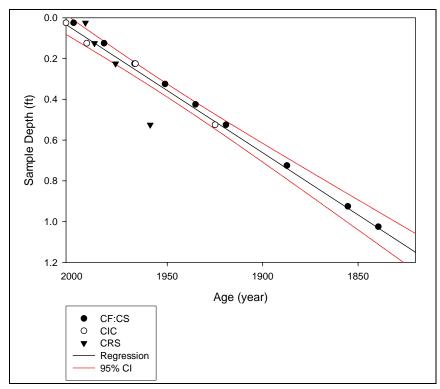


Figure 16. Plot of sediment ages in years derived from three ²¹⁰Pb models for vibracore CMS-SD-4204 with 95 percent confidence interval.

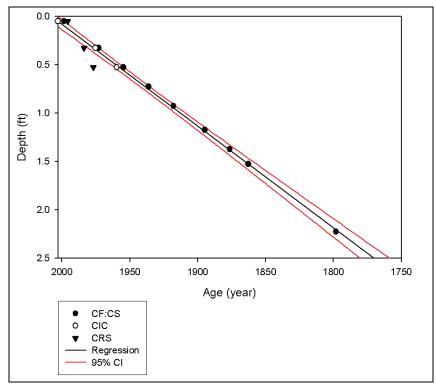


Figure 17. Plot of sediment ages in years derived from three ²¹⁰Pb models for vibracore CMS-SD-4206 with 95 percent confidence interval.

Sediment age dating using 137Cs

Introduction

An artificial radioactive isotope, ¹³⁷Cs, is a worldwide fallout product of atmospheric nuclear weapons testing, which began in 1954 and peaked in 1963 (Appleby et al. 1991). A more recent source of ¹³⁷Cs deposition is from the accident at the Chernobyl nuclear reactor in 1986 and is primarily confined to Europe (Appleby and Smith 1993). The half-life of ¹³⁷Cs is 30 years (Appleby et al. 1991).

Because terrestrial ¹³⁷Cs is strongly bound to sediment, ¹³⁷Cs directly enters the fluvial environment from atmospheric fallout. The residence time of ¹³⁷Cs in the water column is less than 2 years (Edgington and Robbins 1976).

Previous research

Abril (2004) discusses the limitations of using ¹³⁷Cs as a time marker to support the CRS and Sediment Isotope Tomography (SIT) models. The SIT model, not used in this research, allows for the interpretation of ²¹⁰Pb profiles, which result when both sediment accumulation rates and the ²¹⁰Pb fluxes vary with time (Abril 2004). Usually, the 1953 and 1963 periods of ¹³⁷Cs deposition are used to validate ²¹⁰Pb models. Abril (2004) observed that this relatively simple method of correlation does not support CRS or SIT chronology if the derived sedimentation rates cannot explain the entire ¹³⁷Cs activity profile without postulating mixing. He also points out that the ¹³⁷Cs 1953 and 1963 time markers for a given CRS and SIT chronology cannot be considered definite if other dating models can equally explain the entire data set and produce a different chronology.

Mitchell et al. (1983) applied the ¹³⁷Cs technique to estimate the amount of erosion and sediment deposition within two watersheds, their waterways, and reservoir in Monticello, IL. Their research identified accumulation of ¹³⁷Cs in sediment and soil samples as a measurement of sediment movement.

Appleby et al. (1995) used results from ¹³⁷Cs and ²¹⁰Pb dating of lake sediments to explain a rise in atmospheric temperature. Radiometric dating revealed significant increase in sediment accumulation after 1950. As a result of this research, Appleby et al. (1995) found that dense organic sedi-

ment layered in the sediment record is possibly associated with inwash or slump event. Appleby et al. (1995) interpreted the slump events as a result of recent climate warming, which in turn lead to greater erosion and subsequent input into the sediment column.

Application of 137Cs dating methods

Once ¹³⁷Cs enters a fluvial environment, it is rapidly removed from the water column onto the sediment bed. The Chernobyl accident confirms this observation: 75 percent of Chernobyl radiocesium deposited during May 1986 had been eliminated from the water column by November 1986 (Santschi et al. 1988).

The specific activity of ¹³⁷Cs in soils varies according to land use (Bierman 1998). The ¹³⁷Cs isotope enters fluvial environments by precipitation or transport from erosion and strongly adsorbs to organics and fine-grained sediments. Movement of ¹³⁷Cs from the site of deposition is due largely to erosional processes of the soil (McHenry et al. 1978). The structured pattern shown by the curve for ¹³⁷Cs concentration in most sediments investigated indicates that faunal mixing of the surface muds does not destroy the vertical stratification of the sediment profile (Pennington 1976). Davis et al. (1984) observed that the occurrence of ¹³⁷Cs at pre-fallout sediment depths is due mostly to net downward molecular diffusion and adsorption, and that surface concentration is due to net upward diffusion and adsorption, recycling of sedimentary ¹³⁷Cs in the water column, and delayed input from the watershed.

While ²¹⁰Pb is used to date an entire sediment column with accumulation in the last 150 years, ¹³⁷Cs is an event marker, used only for specific dates of 1954, the onset of ¹³⁷Cs fallout, and 1963, the peak ¹³⁷Cs fallout. Plots of ¹³⁷Cs are made directly from the activity of the laboratory analysis. Appleby et al. (1993) described the value of comparing ¹³⁷Cs and ²¹⁰Pb: first, because the response of ²¹⁰Pb to transport processes may be different from that of ¹³⁷Cs, comparisons between the two will be helpful in validating the model and, secondly, because radionuclide inventories may be affected by e.g., sediment focusing, normalization of ¹³⁷Cs inventories against ²¹⁰Pb will to some extent allow an elimination of the effects of such processes. Discrepancies between ²¹⁰Pb and ¹³⁷Cs are perhaps due to the downward migration of ¹³⁷Cs in the sediment column. Figure 18 through Figure 22 show ²¹⁰Pb profiles with the ¹³⁷Cs 1963 date.

Laboratory analysis methods

Detection of ¹³⁷Cs is by gamma ray spectroscopy using high purity germanium detectors with high-resolution spectrometry. Unlike ²¹⁰Pb analysis, no chemical separation is needed. Specific activities of ¹³⁷Cs are calculated using a counting efficiency curve derived by analyzing multiple nuclide standards prepared in the same counting geometry (Teledyne 2004). Teledyne (2004) described the standard geometry used for gamma counting, including 1-L wrap-around Marinelli containers, 300 mL or 150 mL bottles, charcoal cartridge or 2-in. filter paper source geometry. Calibration and counting efficiencies of the gamma counting system for these geometries are determined with standard (known) radionuclide activity traceable to the National Institute of Standards and Technology (Teledyne 2004).

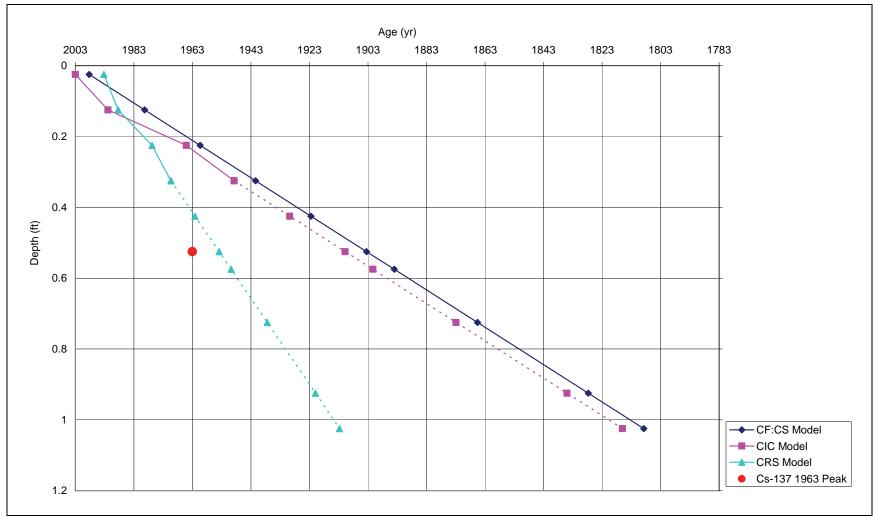


Figure 18. ²¹⁰Pb and ¹³⁷Cs chronology of vibracore CMS-SD-4204. Dashed line indicates extrapolated years.

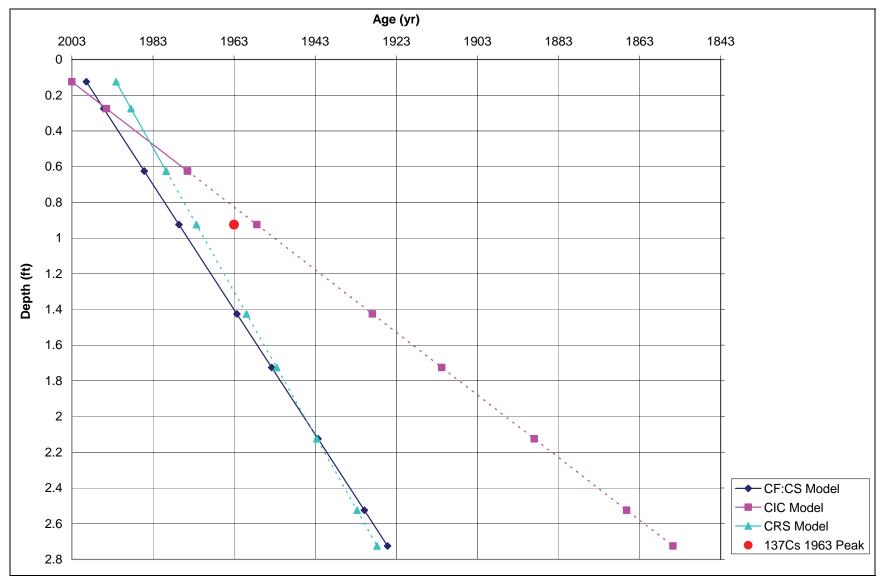


Figure 19. ²¹⁰Pb and ¹³⁷Cs chronology of vibracore CMS-SD-4209. Dashed line indicates extrapolated years.

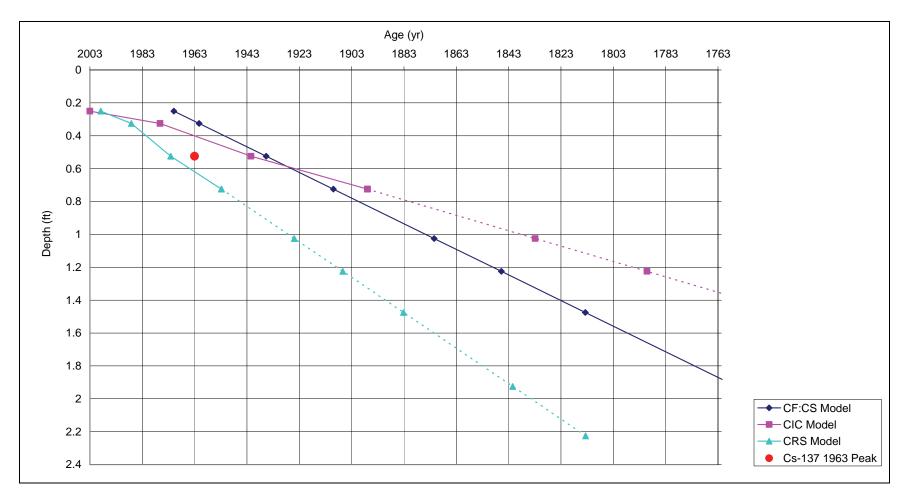


Figure 20. ²¹⁰Pb and ¹³⁷Cs chronology of vibracore CMS-SD-4212. Dashed line indicates extrapolated years.



Figure 21. ^{210}Pb and ^{137}Cs chronology of vibracore CMS-SD-4213. Dashed line indicates extrapolated years.

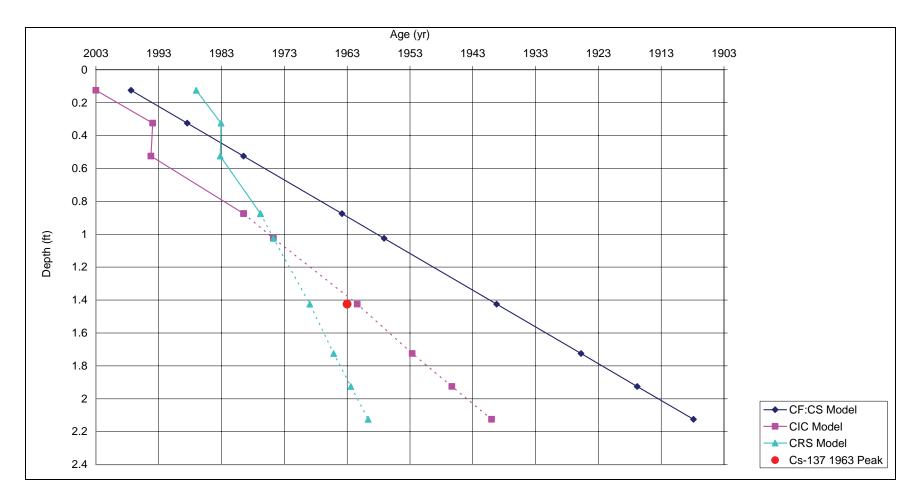


Figure 22. ²¹⁰Pb and ¹³⁷Cs chronology of vibracore CMS-SD-4218. Dashed line indicates extrapolated years.

137Cs chronology

Vibracores CMS-SD-4204, CMS-SD-4209, CMS-SD-4210, CMS-SD-4212, CMS-SD-4213, and CMS-SD-4218 all displayed prominent ¹³⁷Cs peaks, indicating negligible sediment mixing in these areas (Figure 23 through Figure 27). The ¹³⁷Cs profile of the vibracore closest to the dam, CMS-SD-4222, does not have a ¹³⁷Cs peak perhaps as the result of the dam breach or influence from the dam itself on fluctuation of sediment deposition. In addition to CMS-SD-4222, neither CMS-SD-4206 nor CMS-SD-4219 vibracores displayed ¹³⁷Cs peaks.

Figure 18 through Figure 22 are plots of age versus depth for the ²¹⁰Pb models and the 1963 ¹³⁷Cs peak for vibracores CMS-SD-4204, CMS-SD-4209, CMS-SD-4212, CMS-SD-4213, and CMS-SD-4218. In CMS-SD-4204, the CF:CS model and CIC model are in close agreement. However, the ¹³⁷Cs peak does not correlate well with these two models. In CMS-SD-4209, ¹³⁷Cs peak lies closest to the CIC model and in CMS-SD-4212, the ¹³⁷Cs peak is closest to the CRS model. In the remaining vibracores plotted in these figures, the ¹³⁷Cs tracks the age results of the CF:CS model closer than the CIC or CRS models.

Two cores, GM-105 and GM-305, taken in floodplain deposits at the Greystone Mill site yielded enough activity to identify the 1963 peak at 5 in. and 3 in., respectively (Figure 28 and Figure 29). Minor ¹³⁷Cs peaks are seen in sediment cores GM-505 and GM-605, located on the east bank of the suspected raceway of the Revolutionary War Powder Mill (Figure 30 and Figure 31).

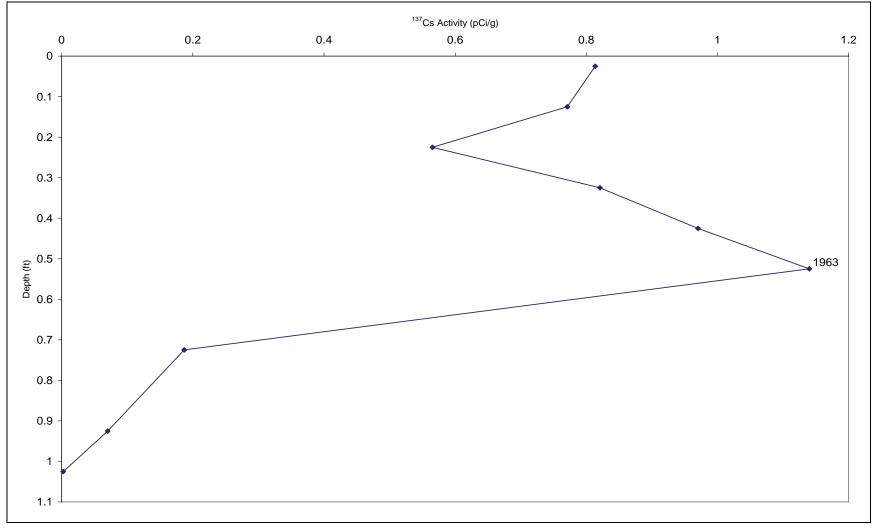


Figure 23. ¹³⁷Cs activity at sampled depth from surface in vibracore CMS-SD-4204. The 1963 peak indicates the year recorded as producing the highest ¹³⁷Cs fallout from nuclear testing.

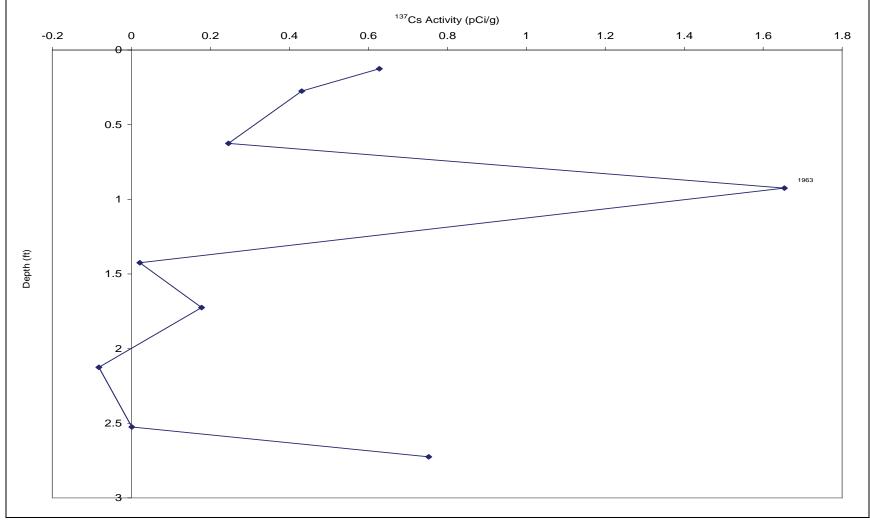


Figure 24. ¹³⁷Cs activity at sampled depth from surface in vibracore CMS-SD-4209. The 1963 peak indicates the year recorded as producing the highest ¹³⁷Cs fallout from nuclear testing.

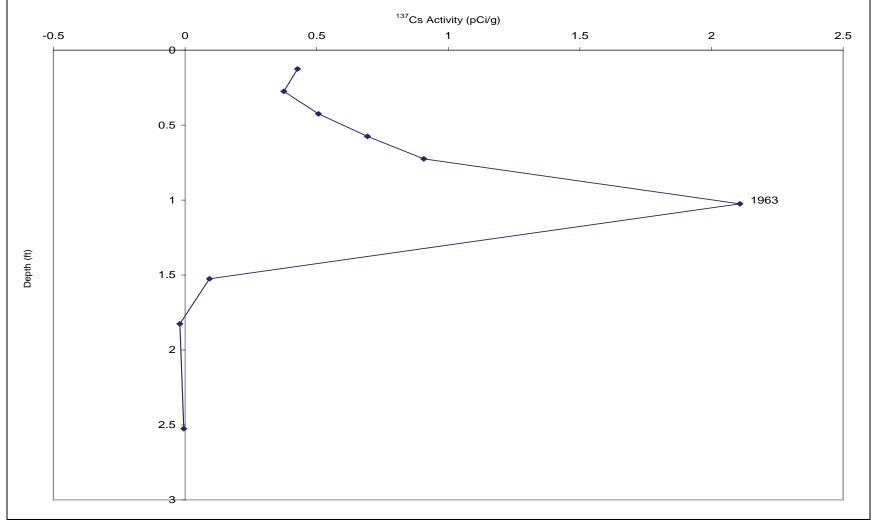


Figure 25. ¹³⁷Cs activity at sampled depth from surface in vibracore CMS-SD-4210. The 1963 peak indicates the year recorded as producing the highest ¹³⁷Cs fallout from nuclear testing.

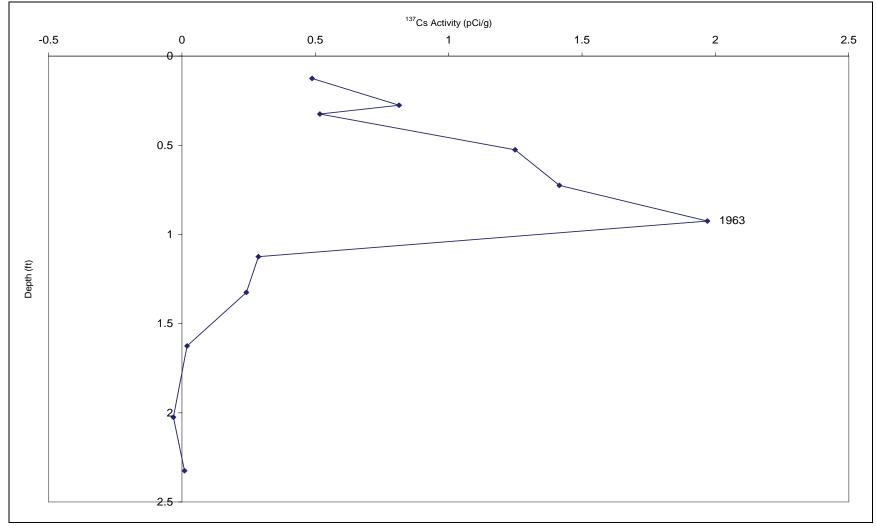


Figure 26. ¹³⁷Cs activity at sampled depth from surface in vibracore CMS-SD-4213. The 1963 peak indicates the year recorded as producing the highest ¹³⁷Cs fallout from nuclear testing.

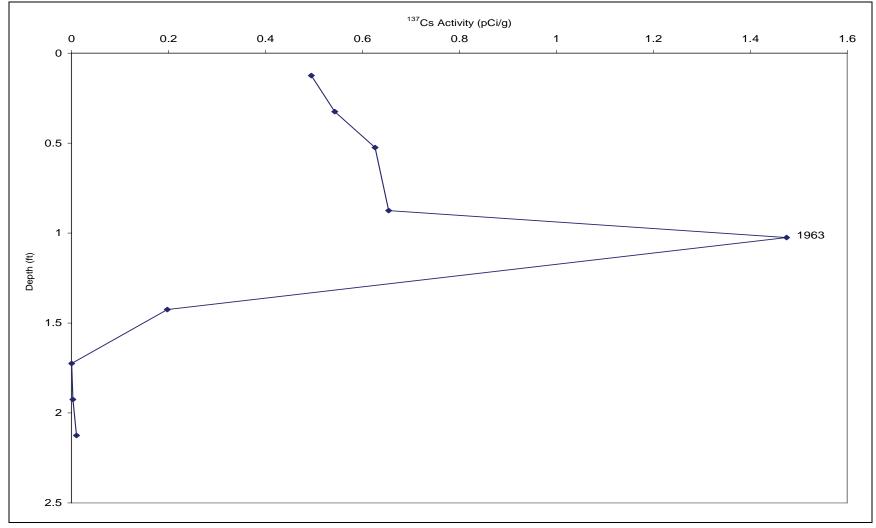


Figure 27. ¹³⁷Cs activity at sampled depth from surface in vibracore CMS-SD-4218. The 1963 peak indicates the year recorded as producing the highest ¹³⁷Cs fallout from nuclear testing.

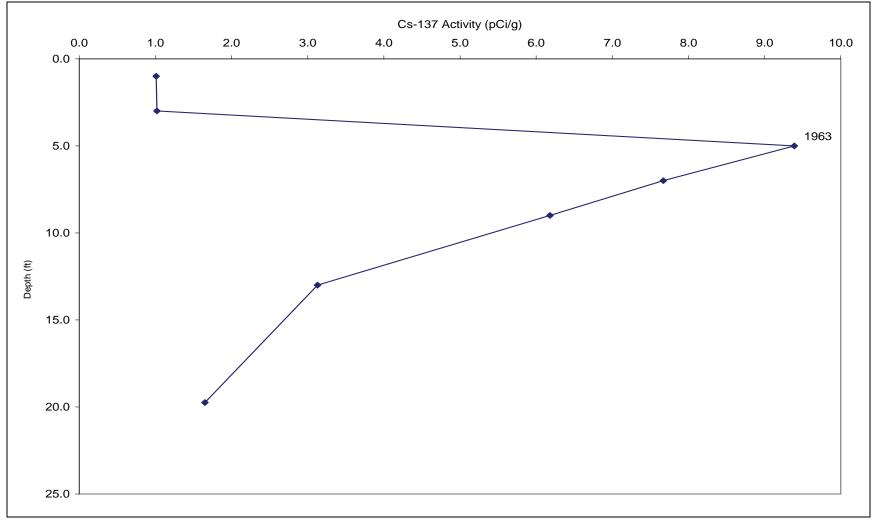


Figure 28. ¹³⁷Cs activity in sediment core GM-105, Greystone Mill. The 1963 peak indicates the year recorded as producing the highest ¹³⁷Cs fallout from nuclear testing.

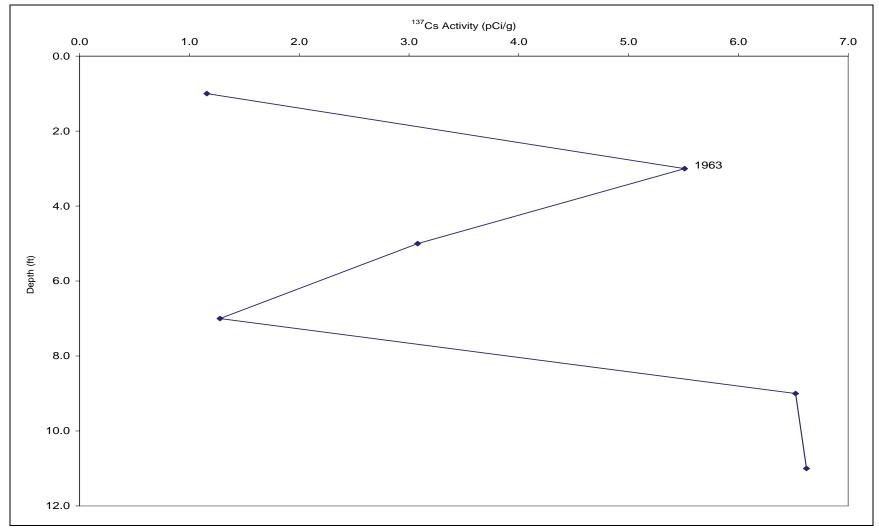


Figure 29. ¹³⁷Cs activity in sediment core GM-305, Greystone Mill. The 1963 peak indicates the year recorded as producing the highest ¹³⁷Cs fallout from nuclear testing.

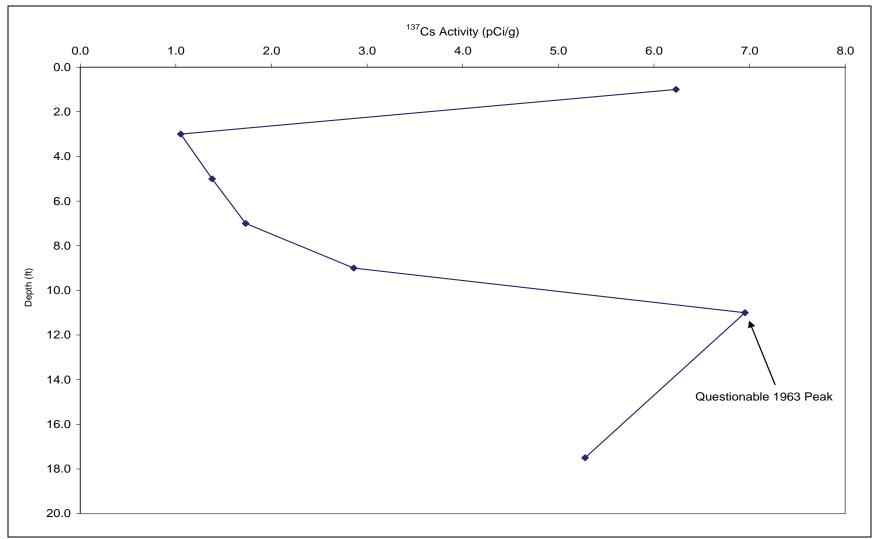


Figure 30. ¹³⁷Cs activity in sediment core GM-505, Greystone Mill.

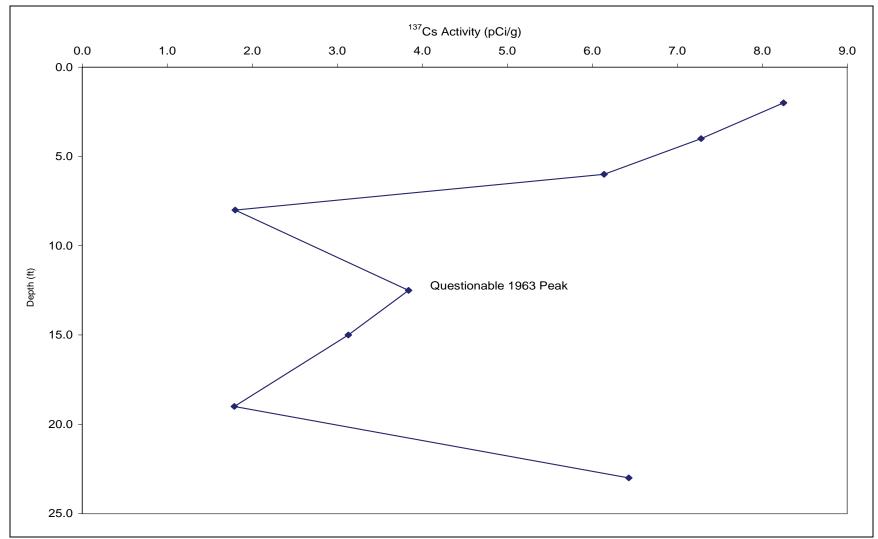


Figure 31. ¹³⁷Cs activity in sediment core GM-605, Greystone Mill.

5 Gunpowder

Introduction

Brief history of gunpowder in Rhode Island

Prior to the Revolutionary War, the few powder mills that existed produced minor amounts of gunpowder making the Colonies greatly dependent on England for much of the powder used in ammunition. Once the war began, imported supplies were discontinued and the Colonies started manufacturing gunpowder out of necessity. In 1776, the Revolutionary War Powder Mill was constructed along the west bank of the Woonasquatucket River in Johnston, RI (Figure 1).

The powder mill took advantage of an existing water wheel constructed for a sawmill known as Mudd Mill, operating on the opposite side (east bank) of the river, and the relatively close proximity to the magazine in Providence, RI, where the gunpowder was to be stored. A dam and mill pond to operate the waterwheel, which in turn powered the machinery, were already in place.

On August 28, 1779, the Revolutionary War Powder Mill received a load of powder, deemed unfit because of dampness, to remanufacture. The practice of remanufacturing the powder into a usable product contained a high risk of explosion. During the process, foreign material other than the known components of gunpowder (potassium nitrate, sulfur, and charcoal) sparked the powder and resulted in a tremendous explosion. At the time of the explosion, there was about two tons of finished powder upon the premises, besides a large amount of powder to be made over (The Observer 1975).

The explosion completely demolished the powder mill. The site remained unchanged until 1785, when a grist mill was built. The grist mill was sold to another operator in 1797 and moved to the east bank of the Woonasquatucket River to be close to Mudd Mill, another property owned by the same operator. Several commercial buildings now occupy the site of the former powder mill.

To determine the presence of gunpowder, a potential tracer in the sediments of this area, pushcores were taken in the vicinity of the former powder mill and were analyzed for sulfur and potassium nitrate. If present in significantly elevated amounts above ambient background levels, these gunpowder components will provide an earlier timeline for soil chronology than radioisotope (Chapter 4) and pollen (Chapter 6) techniques.

No other industry or business is known to have existed that could possibly contribute sulfur or nitrate to the soil above a representative background level. The existence of residue from the mill explosion is a potential aid in dating soils in the study area. Sediment with elevated elemental sulfur and nitrate would indicate deposition after 1779. The gunpowder components, elemental sulfur and nitrate, may be detectable in soils and, therefore, quantified as discussed in the following section.

Composition of gunpowder

The composition of gunpowder is well known, even that from the eighteenth century, and individual components of gunpowder may offer a clue into sediment deposition from this time period. In 1775, the recommendation for making good powder was 75 percent potassium nitrate (saltpeter), 15.5 percent charcoal, and 9.5 percent sulfur (Gilbert 1957) and differed slightly from the nineteenth century formula of 74.5 percent saltpeter, 15.4 percent charcoal, and 10.1 percent sulfur (The Observer 1975). Potassium nitrate acts as an oxidizer to provide extra oxygen as the charcoal ignites and sulfur is the element that ensures a stable reaction.

Powder mill owners rarely made their own potassium nitrate but instead relied on regular producers. Because there were few known natural deposits in the United States, potassium nitrate commonly was made from vegetable and animal refuse in the eighteenth century (Gilbert 1957) but was unfit for immediate use because of impurities. Because the quality of the gunpowder depended upon the purity of the saltpeter, the mills refined it by placing the crude saltpeter into a vat, covering it with water, and boiling the mixture over a low fire until all the saltpeter was dissolved. This procedure was repeated as often as necessary to remove any remaining saltpeter. After the solution was strained and allowed to crystallize, a fine, white substance remained as usable saltpeter.

The charcoal component of gunpowder had to be soft enough not to scratch metal and could not produce any smoke. In addition, the best

charcoal to use in gunpowder is that which can be finely divided, absorbs little moisture from the air, is readily flammable, and leaves little ash after combustion (Gilbert 1957). Considering these requirements, charcoal was produced from light woods, usually willow, black alder, or dogwood. The bark was stripped off, and the wood, instead of being burned in coal pits, was prepared in iron cylinders (The Observer 1975).

Elemental sulfur used to make gunpowder in Colonial America (Gilbert 1957) may have come from domestic sources, or more likely, imported from Europe. St. Clair (1977) states that ironmaking was the only mineral industry widely developed in the colonies through the eighteenth century. Deposits of sulfur from Sicily supplied the needs of Europe and North America for several centuries, up until the middle 1800s (Wessel 1994). Descriptions of sulfur deposits in the United States, for example, Bates (1960) and Wessel (1994) make no mention of native sulfur occurrences in the northeastern part of the country. Powder mills refined the sulfur similar to the method used in the refinement of saltpeter.

After the charcoal and sulfur had been prepared, they were individually pulverized by wheels to form a fine powder suitable for mixing into gunpowder (Gilbert 1957). After the initial mixing, the three ingredients in gunpowder were then proportioned according to a predetermined formula. The incorporation of potassium nitrate, sulfur, and charcoal was usually accomplished using a mortar and pestle. The risk of explosion increased if the mixture became dry, so urine or water was constantly added to the mixture so that it remained moist.

Sulfur and nitrate as indicators of gunpowder

Sulfur, often known as brimstone, is Latin for "burning stone" (Davis and Detro 1992). Because of its combustible properties, sulfur is a key component of gunpowder. Sulfur is insoluble in water and the sulfur sprayed onto the soil surface from the powder mill explosion could possibly still be evident more than 200 years later.

The sulfur cycle in soils is complex, resulting in variability of sulfur forms associated with different ecosystems. According to Brady (2002), the four major forms of sulfur are sulfides, sulfates, organic sulfur, and elemental sulfur (S⁰). Many sulfur compounds are produced in soil but because they are susceptible to decomposition, they do not accumulate and are not readily detected (Freney et al. 1966).

The sulfur oxidation states, sulfate, elemental sulfur, and sulfide, are stable within the stability limits of water (Bohn et al. 1985). Elemental sulfur is oxidized to sulfate primarily by microorganisms. The oxidation rate is determined by the microbial population, particle size of S⁰, soil properties, and environmental conditions, such as temperature and soil moisture content (Zhao 1996). Bohn et al. (1985) notes that S⁰ is stable only under acid conditions and is much less stable than elemental nitrogen. In anaerobic environments with a high level of organic matter, such as a tidal swamp, and those soils that are considered waterlogged, elemental sulfur and other sulfur compounds with lower oxidation states than sulfate can form (Freney and Williams 1983). However, it is important to note that in this type of environment, although sulfite, thiosulfate, and elemental sulfur may occur, usually sulfides make up the greater proportion of the reduced compounds (Freney and Williams 1983).

The sulfur used in manufacturing gunpowder is native or elemental sulfur, a form found in salt domes, volcanic deposits, and in some deposits of calcite, gypsum, and anhydrite (Environmental Secretariat 1977). Volcanoes and fumaroles are also geochemical sources of atmospheric SO_2 and H_2S , and provide lesser quantities of S^0 , SO_3 , and SO_4^{2-} particles (Brown 1982).

Research on sulfur content of soils focuses mainly on the contribution of sulfur to agriculture. In well drained, well aerated soils, most of the sulfur in shallow or surface soil horizons is in organic forms (Freney and Williams 1983). In the same type of environment, elemental sulfur, sulfides, and most other inorganic sources of sulfur that do exist are eventually oxidized to sulfate, which is the usual end product of sulfur metabolism in soils (Gleen and Quaster 1953).

Because sulfur must first be oxidized to sulfate for plant absorption, most research has been confined to total organic sulfur or the sulfate fraction of sulfur and neglects elemental sulfur. Total organic sulfur is a measure of different forms and compounds of sulfur (Environmental Secretariat 1977).

Laboratory analysis of total sulfur includes conversion of the sulfur by oxidization to sulfate and to sulfide by reduction; the total of the two fractions is then measured. The rate of oxidation of sulfur to sulfate is dependent on particle size, where the rate of sulfur oxidation increases with decreasing particle size (Burns 1968). The availability of sulfate is limited by the

breakdown of organic material and not by the oxidation of the released sulfur compounds (Burns 1968).

Freney and Williams (1983) noted that the oxidation of elemental sulfur in soil is affected by the population of microorganisms, soil moisture and aeration, soil temperature, soil pH, and particle size. The oxidation of elemental sulfur can greatly increase with the presence of a substantial microbial population. Thiobacillus thiooxidans or heterotrophic organisms produce a marked increase in the initial rate of oxidation (Freney and Williams 1983).

The most rapid oxidation of elemental sulfur takes place at a moisture level near field capacity, i.e., in the soil moisture range that is optimum for the growth of agricultural plants (Freney and Williams 1983). Soil aeration provides oxygen for the oxidation process and is inversely associated with moisture levels. Thus, high moisture content limits the rate of oxidation.

Microbial oxidation of sulfur will occur at temperatures as low as 4°C, but the process is slowed below 10°C (Freney and Williams 1983). Optimum temperatures vary for the different microorganisms involved in oxidation but temperatures between 25°C and 40°C are close to the optimum for most of the organisms (Weir 1975).

Some microorganisms that contribute to the oxidation process thrive in soils with low pH. However, studies on the effects of sulfur on agricultural crops have noted that adding lime to soil to adjust the pH can increase sulfur oxidation, have no effect, or inhibit oxidation (Freney and Williams 1983).

Studies conducted by Weir (1975) have shown that the rate of oxidation is a function of the surface area exposed to microorganisms. Therefore, the smaller the particle size, the greater the surface area and the greater the rate of oxidation (Freney and Williams 1983).

Sulfur input to soil originates from three major sources: mineral weathering, atmospheric deposition, and organic matter decomposition (Brady 1984) and is usually divided into two broad categories; sulfur contained in soil organic matter and inorganic sulfate sulfur, which is plant available. Most of the inorganic sulfur in soil is in the form of sulfate. Organic sulfur is the most abundant form in soils and is primarily the result of organic

matter decomposition whereas inorganic sulfur is derived from a variety of sources.

The conversion of organic sulfur to sulfate by mineralization is essential in supplying nutrition to plants. The mechanisms of sulfur mineralization are largely unknown but microorganisms are almost certainly involved (Brown 1982).

Sulfur enters the soil system from the atmosphere, either directly as dry deposition or dissolved in precipitation water (Nyborg et al. 1977) or indirectly from the uptake of gaseous sulfur compounds by vegetation and their subsequent release to the soil by decomposition (Brown 1982). The contribution of atmospheric sulfur to the soil depends on proximity to industrial areas, marshlands, and the seacoast and is also influenced by the amount of precipitation and prevailing winds. Inorganic sulfur present in the atomsphere exists as gaseous SO_2 and aerosol sulfate SO_4^{2-} , which are produced primarily from coal burning emissions (Edwards 1998). The New England states are characterized by an excess of atmospheric deposition of sulfur originating largely from combustion of fossil fuels (Johnson and Reynolds 1972). However, much of the sulfur is in the form of sulfuric acid (H_2SO_4), where it exists as a sulfate.

The amount of organic sulfur is usually less in deeper horizons than at the soil surface (Halstead and Rennie 1977). This sulfur is usually divided into ester or organic sulfate and carbon-bonded sulfur. A third category, the heterocyclic sulfur compounds, is sometimes recognized (Environmental Secretariat 1977).

Pest control and irrigation water are also known sources of sulfur to sediment. Many fungicides and insecticides contain sulfur in several forms, but the amount of sulfur added to the soil is minimal in comparison to other sources. Irrigation water carries sulfate to the soil and the amount varies considerably depending on crop need and climatic environment.

The largest secondary source of elemental sulfur is petroleum refining and natural gas processing (United States Geological Survey 1999), but it is first separated from H₂S during the refining process through a technique known as the Claus process. The Claus process produces elemental sulfur by burning H₂S in the presence of a catalyst and recovering the sulfur from the resulting vapor as a condensate (United States Department of Labor

2000). Average crude oil contains about 84 percent carbon, 14 percent hydrogen, 1 percent to 3 percent sulfur, and less than 1 percent each of metals, nitrogen, oxygen, and salts (United States Geological Survey 2001).

Soil sampling at Greystone Mill

The powder mill was situated on the west bank of the river across from the east bank positioned Greystone Mill (Figure 1). Aerial photography shows what seems to be an abandoned channel, but the channel appears too straight to be a natural river channel of the Woonasquatucket River. It is possible that this straight channel, which extends parallel to the present channel of the Woonasquatucket River, is the raceway of the former Revolutionary War Powder Mill.

Seventeen cores were taken in the Adrian muck, the soil on which the powder mill possibly existed, with 2.0-in. (inside diameter) PVC pipe cut to lengths of 41 in. Samples were also extracted using a pushcore from the floodplain of the Woonasquatucket River in the area of the former Revolutionary War Powder Mill. Although soil recovery was better using the pushcore, the extraction method used did not appear to influence the sulfur or nitrate laboratory analysis. Of the 18 cores, eight were selected for sulfur and nitrate analyses. The cores and sample interval selected for the nitrate and sulfur analyses and the results of the analyses are in Table 8.

The area where the cores were taken supports little or no vegetation. It is apparent that this area ponds water from precipitation and, because this area serves as the floodplain of the Woonasquatucket River, it may also receive water from the river channel during flood events. It is important to note, however, that because of the number of dams and reservoirs upstream from this site, the water flow is carefully controlled and flooding of this area from river overflow is at most, a rare occurrence.

Classification of soils at Greystone Mill

The samples taken at Greystone Mill lie within a hydric soil classified as the Adrian muck (Aa) of the Adrian series, a poorly drained soil formed in herbaceous organic material over sandy deposits on outwash plains, lake plains, lake terraces, floodplains, moraines, and till plains (United States

Table 8. Level of nitrate and elemental sulfur in Greystone Mill samples.

Geoprobe No.	Sample Interval fro Top of Core (in.)	Mitrate (ppm)	Elemental Sulfur (ppm)
GM-2	0.0-5.0	13.1	2220
GM-2	5.0-9.0	13.5	702
GM-3	0.0-4.5	7.49	2390
GM-3	4.5-8.0	2.08	1030
GM-4	0.0-4.5	8.71	2940
GM-4	4.5-9.0	2.31	748
GM-5	0.0-5.3	3.35	713
GM-5	5.3-10.0	5.1	1380
GM-6	0.0-10.0	76.6	1020
GM-6	10.0-17.0	21.3	932
GM-6	17.0-25.0	1.09	341
GM-7	0.0-5.0	3.8	269
GM-7	5.0-10.0	NDa	180
GM-7	10.0-16.0	NDa	100
GM-8	0.0-4.2	16.1	3160
GM-8	4.2-8.5	5.65	817
GM-9	0.0-0.9	9.2	497
GM-9	0.9-14.0	1.54	212
GM-9	14.0-17.0	NDa	81
GM-10	0.0-0.6	NDa	6700
GM-10	0.6-10.0	11.5	1870
GM-20	0.0-3.8	4.35	1690
GM-20	3.8-4.0	10.1	834
GM-21	0.0-4.0	44.7	4550
GM-21	4.0-8.0	NDa	2230
GM-105	0.0-2.0		1990
GM-105	2.0-4.0		2250
GM-105	4.0-6.0		2340
GM-105	6.0-8.0		2260
GM-105	8.0-10.0		1330
GM-105	10.0-12.0		933
GM-105	12.0-14.0		369
GM-105	14.0-16.0		431
GM-105	16.0-18.0		274
GM-105	18.0-21.5		390

Geoprobe No.	Sample Interval from Top of Core (in.)	Nitrate (ppm)	Elemental Sulfur (ppm)
GM-205	0.0-3.0		2140
GM-205	3.0-5.0		3770
GM-205	5.0-7.0		3330
GM-205	7.0-9.0		3270
GM-205	9.0-11.0		1420
GM-205	11.0-13.0		2170
GM-205	13.0-15.0		2000
GM-205	15.0-17.0		387
GM-205	17.0-20.0		384
GM-305	0.0-2.0		3500
GM-305	2.0-4.0		3500
GM-305	4.0-6.0		3090
GM-305	6.0-8.0		1640
GM-305	8.0-10.0		1810
GM-305	10.0-12.0		1030
GM-305	12.0-14.0		1730
GM-305	14.0-16.0		1040
GM-305	16.0-19.0		910
GM-405	0.0-2.0		3440
GM-405	2.0-4.0		2730
GM-405	4.0-6.0		2320
GM-405	6.0-8.0		4010
GM-405	8.0-10.0		1490
GM-405	10.0-12.0		299
GM-405	12.0-15.0		787
GM-505	0.0-2.0		1010
GM-505	2.0-4.0		970
GM-505	4.0-6.0		1390
GM-505	6.0-8.0		2310
GM-505	8.0-10.0		1830
GM-505	10.0-12.0		1680
GM-505	12.0-14.0		1090
GM-505	14.0-16.0		753
GM-505	16.0-19.0		661
GM-605	0.0-3.0		1550
GM-605	3.0-5.0		1080

Geoprobe No.	Sample Interval from Top of Core (in.)	Nitrate (ppm)	Elemental Sulfur (ppm)
GM-605	5.0-7.0		1200
GM-605	7.0-9.0		944
GM-605	9.0-11.0		790
GM-605	11.0-14.0		681
GM-605	14.0-16.0		480
GM-605	16.0-18.0		271
GM-605	18.0-20.0		135
GM-605	20.0-22.0		113
GM-605	22.0-24.0		62
GM = Greystone Mill			
aND = Non-Detect			

Department of Agriculture 1981). Typically, the surface layer is black muck 20 in. thick (United States Department of Agriculture 1981), as found at the Greystone Mill site. Adrian muck is unsuitable for building construction, cultivated crops, or any other urban development. Because of the unsuitable nature of the Adrian muck, it is unlikely that any operations close to Greystone Mill contributed anthropogenic sulfur to the soil. The textile mills relied on waterpower to operate machinery, so the mills are an unlikely source of sulfur.

Soil sampling at Allendale Mill Pond and Lyman Mill Pond

The Allendale Mill Pond and Lyman Mill Pond are located downstream of the former Revolutionary War Powder Mill site. Sulfur is not easily soluble in water so if the elemental sulfur from the explosion is still present, it should be evident in the Allendale Mill Pond and Lyman Mill Pond cores.

In March 2005, 24 vibracores were sampled for elemental sulfur in these mill ponds. The vibracoring technique is described in "Subsurface sampling" in Chapter 3. Because of low levels found in the first phase of the Greystone Mill cores, nitrate was not analyzed in the second phase of Greystone Mill cores or the Allendale Mill Pond and Lyman Mill Pond vibracores. The cores and sample interval selected for the sulfur analysis and the corresponding level of elemental sulfur are in Table 9.

Table 9. Level of elemental sulfur in Lyman Mill Pond and Allendale Mill Pond samples.

Vibracore	Sample Interval From Top of Core (in.)	Elemental Sulfur (ppm)
LPX-SD-4505	2.6-3.0	1340
LPX-SD-4505	3.2-3.4	1140
LPX-SD-4505	3.5-3.8	535
LPX-SD-4505	4.2-4.5	184
LPX-SD-4505	4.7-5.0	93.5
LPX-SD-4507	2.8-3.0	1270
LPX-SD-4507	3.1-3.4	33.7
LPX-SD-4507	3.4-3.7	26.1
LPX-SD-4507	3.7-4.0	19.8
LPX-SD-4507	4.1-4.3	27.5
CMS-SD-4206	0.6-0.7	11300
CMS-SD-4206	0.8-0.9	5060
CMS-SD-4206	2.25-2.35	737
CMS-SD-4209	0.0-0.10	1440
CMS-SD-4209	0.75-0.80	1030
CMS-SD-4209	1.20-1.30	10300
CMS-SD-4209	2.00-2.10	1780
CMS-SD-4209	2.20-2.30	1230
CMS-SD-4209	3.00-3.10	1190
CMS-SD-4210	0.0-0.10	2430
CMS-SD-4210	0.15-0.25	2390
CMS-SD-4210	0.45-0.55	2790
CMS-SD-4210	1.25-1.35	6420
CMS-SD-4210	1.55-1.65	5630
LPX = Lyman Mill Pond		
CMS = Allendale Mill Pond		

Laboratory analysis of sulfur

To detect S⁰, the soil sample is prepared for inductively coupled plasma atomic emission spectrometry (ICP-AES) using United States Environmental Protection Agency Method 3050B (United States Environmental Protection Agency 1996a). For the ICP-AES analysis, hydrochloric acid (HCl) is added to the initial digestate and the sample is refluxed with the final volume of sample diluted to 100 mL (United States Environmental Protection Agency 1996a). Based on United States Environmental

Protection Agency Method 3050B, the sample is homogenized, heated, and reduced to approximately 5 mL of digestate. Ten mL of HCl is added to the digestate, which is then covered with a vapor recovery device and heated at 95° C \pm 5° C for 15 min (United States Environmental Protection Agency 1996a). The digestate is then filtered through Whatman No. 41 filter paper. The filtrate is collected and analyzed using ICP-AES.

The ICP-AES laboratory analysis for S⁰ follows United States Environmental Protection Agency Method 6010B (United States Environmental Protection Agency 1996b). ICP-AES identifies trace elements and metals in samples by using sequential or simultaneous optical systems and axial or radial viewing of the plasma (United States Environmental Protection Agency 1996b) and is a sensitive test that records elemental sulfur only and not any other sulfur fraction. The instrument described by United States Environmental Protection Agency (1996b) measures characteristic emission spectra by optical spectrometry. Element-specific emission spectra are produced by radio frequency inductively coupled plasma and dispersed by a grating spectrometer (United States Environmental Protection Agency 1996b).

Sulfur in Rhode Island

There is no documentation on sulfur content of Rhode Island soils but personal communication with Turenne (2004) revealed that the sulfur concentrations of the Greystone Mill cores were unusually high. In order to relate the sulfur concentration to a known base level in soils, literature from other states was reviewed to determine if a comparison of soil type and sulfur levels between states is feasible.

Tabatabai and Bremner (1972) studied the sulfur status of Iowa soils to obtain information for evaluation of sulfur deficiency and the requirement of sulfur in soils for satisfactory crop production. Sixty-four surface soils representing the major soil series in Iowa were analyzed for total sulfur. The total sulfur content of the analyzed soils ranged from 57 ppm to 618 ppm (Tabatabai and Bremner 1972). Unfortunately, elemental sulfur was not separated in the analysis.

A study was conducted in the Copper Basin region of Tennessee by Wolt and Lietzke (1982) on the anthropogenic sulfur that was released from copper-sulfide ore smelting operations. Samples were taken downwind of the smelter operations from three similar soils, clayey and fine loamy,

oxidic, and mesic Typic Hapludults. The total sulfur was analyzed and found to be between 1,200 and 1,800 ppm of sulfur per gram of clay for those sites receiving high sulfur input and in those areas with low sulfur input, the soils yielded between 500 and 700 ppm of sulfur per gram of clay (Wolt and Lietzke 1982).

The comparison of the Copper Basin region to the Greystone Mill site is difficult because the elemental sulfur is included in the total organic sulfur measurement. Still, the combined sulfur components in the Copper Basin region are considerably less than the elemental sulfur fraction from many of the Greystone Mill soil samples (Table 8).

It is difficult to establish a base level or background level for elemental sulfur in Rhode Island. Samples were taken from the Adrian muck soil complex at other locations in Rhode Island to determine a base level for sulfur concentration unaffected by the powder mill explosion.

Elemental sulfur concentration is plotted versus depth to visualize a relationship between sulfur levels and sediment age. In order to obtain the appropriate sample size, a composite sample over several inches was used in the analysis. Seven of the samples, GM-2, GM-3, GM-4, GM-8, GM-10, GM-20, and GM-21, showed extraordinarily high levels of sulfur, between 2,000 ppm and 7,000 ppm (Table 8). One sample, GM-10, displayed a high concentration of 6,700 ppm in the upper half-inch of soil. The deepest sample, GM-6, contained a high level of 932 ppm from 0.0 to 10.0 in. and showed several hundred parts per million elemental sulfur in the composite sample from 17 to 25 in. deep.

In addition to the Greystone Mill site, two sites were selected to test for elemental sulfur levels. Because of the location of these additional sites, designated as LM and AW, they are presumed to be unaffected by the powder mill explosion (Figure 1). However, the sulfur levels at the LM site yielded elemental sulfur levels similar to those found at Greystone Mill. The elemental levels for the three sites, Greystone Mill (2004 and 2005 cores), LM, and AW are plotted in Figure 32.

Elemental sulfur levels were also measured in Allendale Mill Pond and Lyman Mill Pond. The highest levels were recorded in vibracore CMS-SD-4206 in Allendale Mill Pond. Figure 33 is the combined plot of the elemental sulfur levels from both ponds.

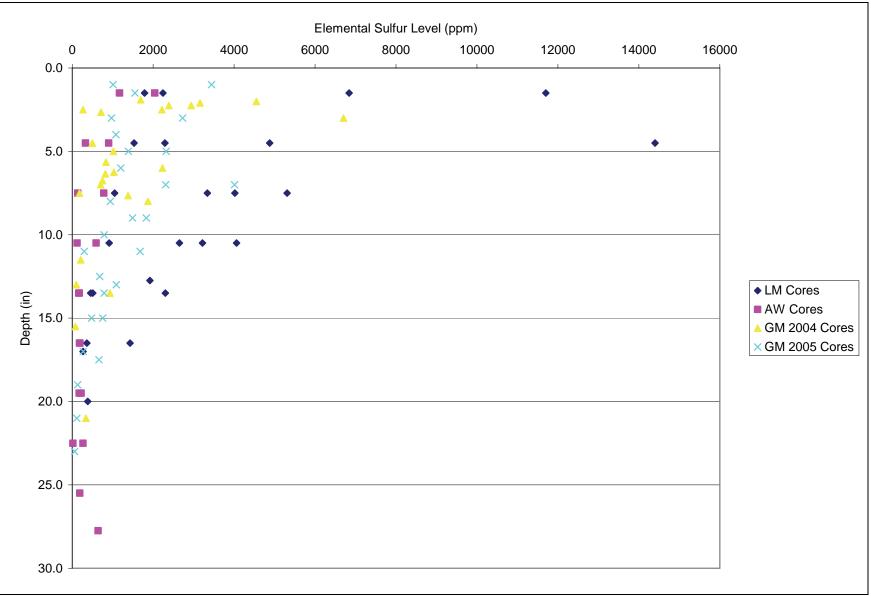


Figure 32. Elemental sulfur levels of Adrian muck at three sites in Rhode Island.

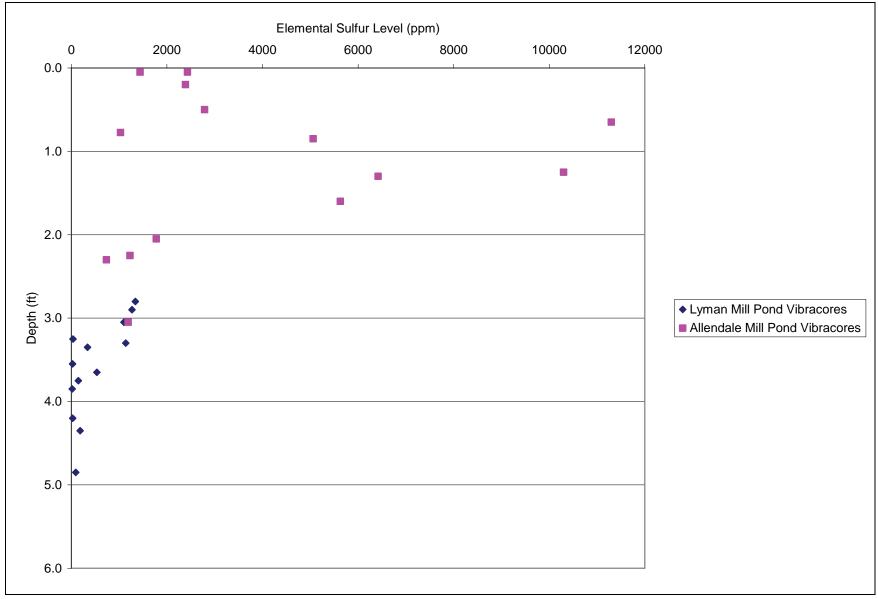


Figure 33. Elemental sulfur levels at Lyman Mill Pond and Allendale Mill Pond.

Nitrates in soils

As in the case of sulfur, research on nitrate contained in soils focuses on agriculture requirements. Nitrogen behaves similarly to sulfur in that plants and microorganisms absorb it as it moves through the soil. Nitrogen is initially released in the form of ammonium from the decomposition of organic material. In soils with a pH of 6.0 to 6.5 ammonium-N (NH4-N) concentrations are typically low because ammonium is rapidly converted to nitrate (Heckman 2003). Accordingly, highly organic soils produce higher levels of nitrate than those soils with little or no organic material. Potassium nitrate (saltpeter) is stable only under oxidizing conditions at pH>3 (Bohn et al. 1985).

Laboratory analysis of nitrates at Greystone Mill

The standard operating procedure for nitrate follows United States Environmental Protection Agency Method 300.0 (United States Environmental Protection Agency 2004) for ion chromatography. Ion chromatography (IC) is a form of liquid chromatography that uses ion-exchange resins to separate atomic or molecular ions and detect inorganic anions based on their interaction with the resin (New Mexico State University 2005). According to United States Environmental Protection Agency (2004), a small volume of sample is introduced into the IC after separation and the anions are measured after traveling through a series of columns and a suppressor device.

As with the sulfur, nitrate concentration is plotted versus depth (Figure 34). Sample GM-6 displayed an unusually high peak in the upper 10 in. of the core.

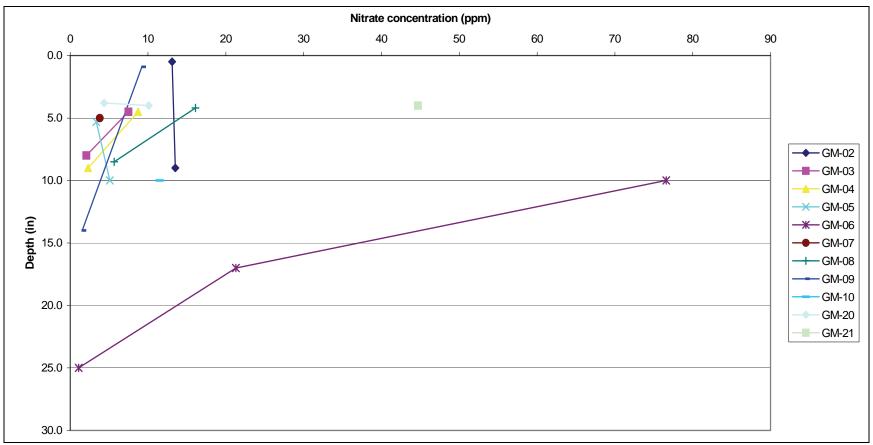


Figure 34. Nitrate concentration of the Greystone Mill cores versus depth.

6 Palynology Analysis

Introduction

Palynology analysis was investigated for use in correlating other sediment age dating methods. Because of laboratory restriction on possibly contaminated sediment in Allendale Mill Pond and Lyman Mill Pond, only samples from Greystone Mill site were used in the palynology study.

Japanese knotweed, *Polygonum cuspidatum*, a dioecious, herbaceous perennial, was introduced from Asia to Europe during the mid-1800s then to the United States in the late nineteenth century (Patterson 1976; Bram and McNair 2004). In 1847, Japanese knotweed was awarded a gold medal by the Society of Agriculture & Horticulture at Utrecht for the most interesting new ornamental plant of the year (Bailey and Conolly 2000). Unfortunately, it quickly spread so that by 1938 information was being published on how to eradicate the plant (New England Wild Flower Society 2004).

Japanese knotweed thrives in areas of disturbed soil, both by natural and human activity, such as riverbanks, and along roads (Beerling et al. 1994; Seiger and Merchant 1997) and spreads vegetatively through rhizomes dispersed in soil transported by human activity or streamflow in river channels.

Leaves are heart shaped with white clusters of male and female flowers, typically on separate plants (Cabi Bioscience 2005). The plant forms a dense shrub that excludes native vegetation and reduces wildlife habitats. In addition to a heavy canopy, the dead stems and leaf litter from the Japanese knotweed are slow to decompose and form a deep organic layer, which prevents native seeds from germinating. The rhizomes of the plant consist of emodin, resveratrol, and polydating and are used in Chinese medicine against infectious hepatitis, burns, snakebite, and many other ailments (Zhao 2005).

Although Japanese knotweed has not been used in palynological studies prior to this research, knowledge of the Japanese knotweed habitat, its distinct pollen, and the approximate time of introduction to the New

England states, indicate the invasive plant may prove to be a viable event marker in subsurface sediment.

Data collection

Pushcores from the floodplain of the Greystone Mill site were used in the palynology analysis. Samples were taken from cores GM-3, GM-4, GM-8, and GM-9 at the Greystone Mill site in 0.80 in. intervals. Other sites could not be used because of laboratory restrictions on possibly contaminated soil.

Methodology of analysis

Approximately 10 g of soil was selected from the 0.80-in. samples. The soil samples are oven-dried for 24 hr and then placed in a beaker with hydrofluoric (HF) acid. Soil remains in the HF for 12 hr and is then neutralized by adding tap water and decanting it. The pH was tested until it reached a neutral reading of 7. The soil is placed into test tubes and then centrifuged. After the soil is settled at the bottom of the test tubes, water is poured off and the soil remains.

The soil is divided between two test tubes and placed in a warm water acid bath with 1 cm of hydrochloric acid (HCl). The HCl and soil mixture is stirred and boiling water is added. The soil sample is once again placed in the centrifuge. Boiling water is added approximately every 5 min until the soil is neutralized. Zinc chloride is then added, mixed with the soil, and placed in the centrifuge. The soil is placed in a 250-ml beaker and 100 ml of distilled water is added. The organic material that floats in this solution is poured into test tubes containing distilled water. The centrifuge procedure is repeated. Once the centrifuge is completed, the soil is stirred after adding acidic acid.

Using a graduated cylinder, a solution of nine parts anhydrite to one part sulfuric acid is made and placed on a warming plate in boiling water. The solution boils for 12 min, centrifuged, and neutralized. The sample is strained and divided into three different grain sizes; >90 microns, 25 to 90 microns, and 10 to 25 microns. Phenol is used to preserve the samples. The grain size of 25 to 90 microns, the grain size thought to contain the most pollen, is used for the palynology study.

Presence of Japanese knotweed at Greystone Mill

Japanese knotweed pollen is present in every core analyzed and is described in the palynological study (Table 10). Though smaller than most

Core	Deepest Occurrence of Japanese Knotweed From Top of Core (in.)	Shallowest Occurrence of Japanese Knotweed From Top of Core (in.)	Total Depth of Core (in.)
GM-3	1.95	1.17	8.97
GM-4	3.9	3.12	10.14
GM-8	4.68	3.9	7.8
GM-9	7.8	7.02	14.04

Table 10. Presence of Japanese knotweed pollen in the Greystone Mill cores.

pollen used in sediment age dating (e.g., oak), the pollen of the Japanese knotweed is distinct in appearance. Figure 35 and Figure 36 are photomicrographs of the Japanese knotweed pollen in cores GM-3 and GM-8, respectively.

The Japanese knotweed pollen in core GM-105 is deeper in the sediment column than the ¹³⁷Cs activity level. This area could possibly have been reworked or inundated during flood events. However, the GM 305 core shows the ¹³⁷Cs 1963 peak higher than the level of the first occurrence of Japanese knotweed pollen.



Figure 35. Japanese knotweed pollen indicated by arrow in core GM-3 at a depth of 3.0 to 4.0 in. Size of pollen is approximately 25 microns.



Figure 36. Japanese knotweed pollen indicated by arrow in core GM-8 at a depth of 0 to 4.0 in. Size of pollen is approximately 25 microns.

7 Results and Conclusions

Introduction

The Woonasquatucket River in North Providence, RI, was instrumental in the American Revolutionary War in the late 1700s and in the advancement of the American Industrial Revolution of the early 1800s. The post-glacial river, once narrow and fast flowing, was engineered to redirect its waters into diversion canals, referred to as raceways, to operate machinery in textile mills. To aid the diversion, dams were strategically placed close to the mills. The river responded to these obstructions by forming mill ponds. The development of mills and mill ponds altered the flow of the Woonasquatucket River and created new sites of sediment deposition.

The river provided an ideal setting for industries, but the close proximity of the mills to the river had serious environmental consequences. By-products from manufacturing were dumped into the river and greatly reduced the water quality and contributed to sediment pollution. Knowledge of sedimentation patterns and the amount of recent sedimentation is needed to respond to scientific advancements in restoration and rehabilitation efforts along the river. To assess the sediment regime, this research identified and described geomorphic features of the Woonasquatucket River valley and surrounding terrain. Sediment age dating methods were also used to identify the areas that have recent sediment accumulations to effectively target likely areas of contamination.

Conventional sediment dating techniques, such as ²¹⁰Pb and ¹³⁷Cs, are useful but statistically limited in assigning an estimated age to sediment older than 150 years. These techniques have traditionally been used only in lacustrine or marine depositional environments, but do have some applicability to the Woonasquatucket River environment. In this research, elemental sulfur and nitrate, components of gunpowder, and pollen from Japanese knotweed are also used to build a better geochronology of riverine sediment deposition.

The study site has been divided into four sections; Greystone Mill Reach, North Allendale Mill Reach, South Allendale Mill Reach, and Lyman Mill Reach (Figure 6). For ease of discussion on sedimentation rates and sediment age dating results, North Allendale Mill Reach and South Allendale Mill Reach Allendale Mill Reach Allendale Mill Reach

dale Mill Reach are combined under Allendale Mill Pond. Table 11 lists the sediment age dating techniques used in each section. The pollen analysis was limited to Greystone Mill samples because of laboratory restrictions on conducting a pollen analysis on potentially contaminated samples known to occur in the other study segments.

Study Segment	²¹⁰ Pb	¹³⁷ Cs	Sulfur (gunpowder component	Nitrate (gunpowder component)	Pollen (Japanese knotweed)	Geomorphic Identification
Greystone Mill	Х	Х	Х	Х	Х	Х
Allendale Mill Pond	Х	Х	Х			Х
Lyman Mill Pond	Х	Х	Х			Х

Table 11. Sediment age dating techniques used at sections in the study site.

Greystone Mill

Radioactive dating using ²¹⁰Pb and ¹³⁷Cs

The floodplain of the Woonasquatucket River on the west bank opposite Greystone Mill, which is the site of the former Revolutionary War Powder Mill, supports negligible amounts of ²¹⁰Pb activity, which are insufficient to produce a geochronology from sediments. Vibracores GM-105 and GM-305 are situated on the west bank of the raceway and not likely affected by the overbank deposition or flood events from the Woonasquatucket River. The east bank raceway cores, GM-505 and GM-605, display decreasing ¹³⁷Cs activity with depth (Figure 30 and Figure 31). The prominent 1963 ¹³⁷Cs peaks from GM-105 and GM-305 indicate minor, if any, reworking of sediment at these locations. As evident from the slight ¹³⁷Cs peaks and the depth of these peaks, the east bank of the raceway is influenced by the river to a greater extent than the west bank. Interpretation of the ¹³⁷Cs activity indicates approximately 7 in. of additional sediment has accumulated on the east bank as compared to the west bank of the raceway since 1963. The ¹³⁷Cs activity also indicates that the floodplain of the Woonasquatucket River supports recent (post-1963) deposition.

Sediment deposition sites

As evident from aerial photography, the suspected raceway of the Revolutionary War Powder Mill supported water several times during the twentieth century. The east bank of the raceway is in contact with the river during flood events. During these events, overbank deposition contributes to the sediment column on the east bank of the raceway, an interpretation

supported by the delineation of floodplain deposits in the geomorphic assessment and the ¹³⁷Cs interpretation.

Elemental sulfur

Levels of elemental sulfur, much higher than levels of sulfur in soils of other states for which data are available, exist in the Adrian muck along the west bank of the Woonasquatucket River at the former site of the Revolutionary War Powder Mill. In general, the total sulfur content of up to 5,000 ppm in peat and swamp soils (Freney and Williams 1983). Other than the explosion of the Revolutionary War Powder Mill, there is no known local anthropogenic source, past or present that could contribute to such high levels of elemental sulfur. Furthermore, laboratory analysis detected elemental sulfur, the type found in gunpowder, and did not include sulfate or total sulfur in the analysis. However, other sites assumed not to be influenced by the powder mill explosion because of their distance from the former powder mill also yielded similar high levels of elemental sulfur.

Several explanations for the high sulfur concentrations in the samples exist. There may be an existing unrecognized source of anthropogenic elemental sulfur that has contributed to the sulfur in the soils. It is also possible that the elemental sulfur from the Revolutionary War Powder Mill explosion cannot be separated from the elemental sulfur found in the complex sulfur cycle. Although the laboratory analysis conducted for this research was selected to test for the elemental sulfur component of gunpowder it may be that the elemental sulfur from 1779 could not readily be separated and identified.

A more probable explanation is that the high level of sulfur concentration indicates an unusually high oxidation level of elemental sulfur. The laboratory analysis conducted on samples taken at sites supposedly unaffected by the powder mill explosion showed a wide range of elemental sulfur concentrations.

Potassium nitrate

Potassium nitrate is soluble in water but was detected in the cores from the first sampling event. Only one core, GM-6, yielded an unusually high nitrate concentration. Because of the lack of a discernable timeline in using nitrates, the remainder of the cores was not tested for this element.

Japanese knotweed

Japanese knotweed pollen proved a distinct event marker. Using the known introduction of Japanese knotweed of 1860s to 1880s in the New England states, the first appearance of Japanese knotweed pollen in the samples is correlated to the mid- to late-1800s time period. The presence of the pollen is plotted with the ¹³⁷Cs in Greystone Mill for validation (Figure 37). As shown in the plot, the earliest occurrence of Japanese knotweed lies stratigraphically below the ¹³⁷Cs 1963 activity peak in cores GM-305 and GM-405.

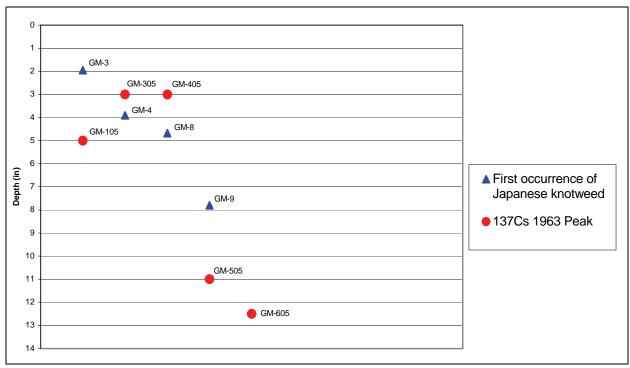


Figure 37. Correlation between the first occurrence of Japanese knotweed and ¹³⁷Cs at Greystone Mill.

As previously discussed, the ¹³⁷Cs 1963 activity for cores GM-505 and GM-605 is considered minor activity and is, therefore, thought to be of questionable reliability an event marker in these cores. The Japanese knotweed pollen, however, proved a prominent marker in the Greystone Mill sediments. The anomalous sediment depth from cores GM-505 and GM-605, which indicated sediment marker depths approximately 3 in. deeper than other cores is, therefore, discounted when interpreting sediment age depths at the Greystone Mill site.

Allendale Mill Pond

The most reliable sediment age dating with ²¹⁰Pb and ¹³⁷Cs was achieved at Allendale Mill Pond. The pond contains high levels of organics with fine-grained sediments, ideal for adsorption of ²¹⁰Pb and ¹³⁷Cs. Based on the activity level and prominent peaks of ¹³⁷Cs in vibracores CMS-SD-4213 and CMS-SD-4218, the Allendale Mill Dam breach in 1991 had a negligible effect on the sediment deposited prior to the breach.

Overall, two ²¹⁰Pb models yielded similar average sedimentation rates for Allendale Mill Pond; 0.026 ft/year using the CF:CS model and 0.050 ft/year calculated from the CRS model. In the CF:CS model, the sedimentation rate is assumed to be constant; an ideal setting that is never achieved. In general, the CIC and CRS models could only be applied to a depth of 0.55 ft with 1962 as the oldest date calculated for this depth interval. A linear extrapolation is used to estimate sediment dates beneath this depth. These numbers are used in plotting the ²¹⁰Pb and ¹³⁷Cs chronology and should not be considered as ²¹⁰Pb dates but rather as extrapolated estimates at best. Sediment accumulation rates for each vibracore using the CF:CS and CRS models are shown in Table 12.

Figure 38 is a hypsometric map that visually represents accumulated sediment in Allendale Mill Pond over a 60-year period (1938 to 1998). Depth data calculated for each vibracore using the CF:CS method comprise the Z-axis (the vertical axis). The varicolored surface shown in each frame of Figure 38 represents the surface of the lake bottom as it would have appeared in that year, according to the CF:CS computations. The blue line at the top of each frame is the lake surface in May 2003, the time the vibracores were taken. The lake surface is the datum and is assigned a depth of 0 (zero). Depths on the Z-scale are in feet and are negative, indicating depth below lake surface. The Z-scale is the same in each frame. Depth values consist of the depth within the vibracore (from the CF:CS computations) plus the water depth at the location of the vibracore. The purple line is the position of Allendale Mill Dam. The perspective view in these frames is to the northwest looking from S13E.

Figure 38 shows shallowing of the pond (sedimentation) from 1938 to 1998. Actual depth to the pond bottom at any location is given by the colors and the color scale to the right. Sedimentation was more pronounced near the dam (south area of the pond) as shown by a progression from light green (9.5- to 10-ft depths) to yellow (7- to 7.5-ft depths).

Sedimentation was less in the northern (distal) part of the pond. Depths varied by only 1.0 to 1.5 ft over the 60 years.

Table 12. Sediment accumulation rates for Allendale Mill Pond. Averages (means) for the CRS model are shown in parentheses for each vibracore.

Vibracore	Depth (ft)	CF:CS ft/year	CRS ft/year
CMS-SD-4204	0.0-0.05	0.006	0.033
	0.10-0.15		0.011
	0.20-0.25		0.001
			(0.015)
CMS- SD-4206	0.0-0.10	0.011	0.021
	0.30-0.35		0.008
			(0.014)
CMS- SD-4209	0.10-0.15	0.021	0.037
	0.25-0.30		0.013
	0.20		(0.025)
CMS- SD-4210	0.10-0.15	0.092	0.107
	0.25-0.30		0.088
	0.40-0.45		0.066
			(0.087)
CMS- SD-4212	0.10-0.15	0.008	0.013
CMS- SD-4213	0.10-0.15	0.020	0.129
CMS- SD-4218	0.10-0.15	0.022	0.067
	0.30-0.35		0.043
	0.50-0.55		0.020
			(0.043)
CMS- SD-4222	0.10-0.15	0.025	0.095
	0.20-0.25		0.068
	0.40-0.45		0.051
			(0.069)
Average Sedimentation Accumulation Rate in Allendale Mill Pond		0.026	0.050

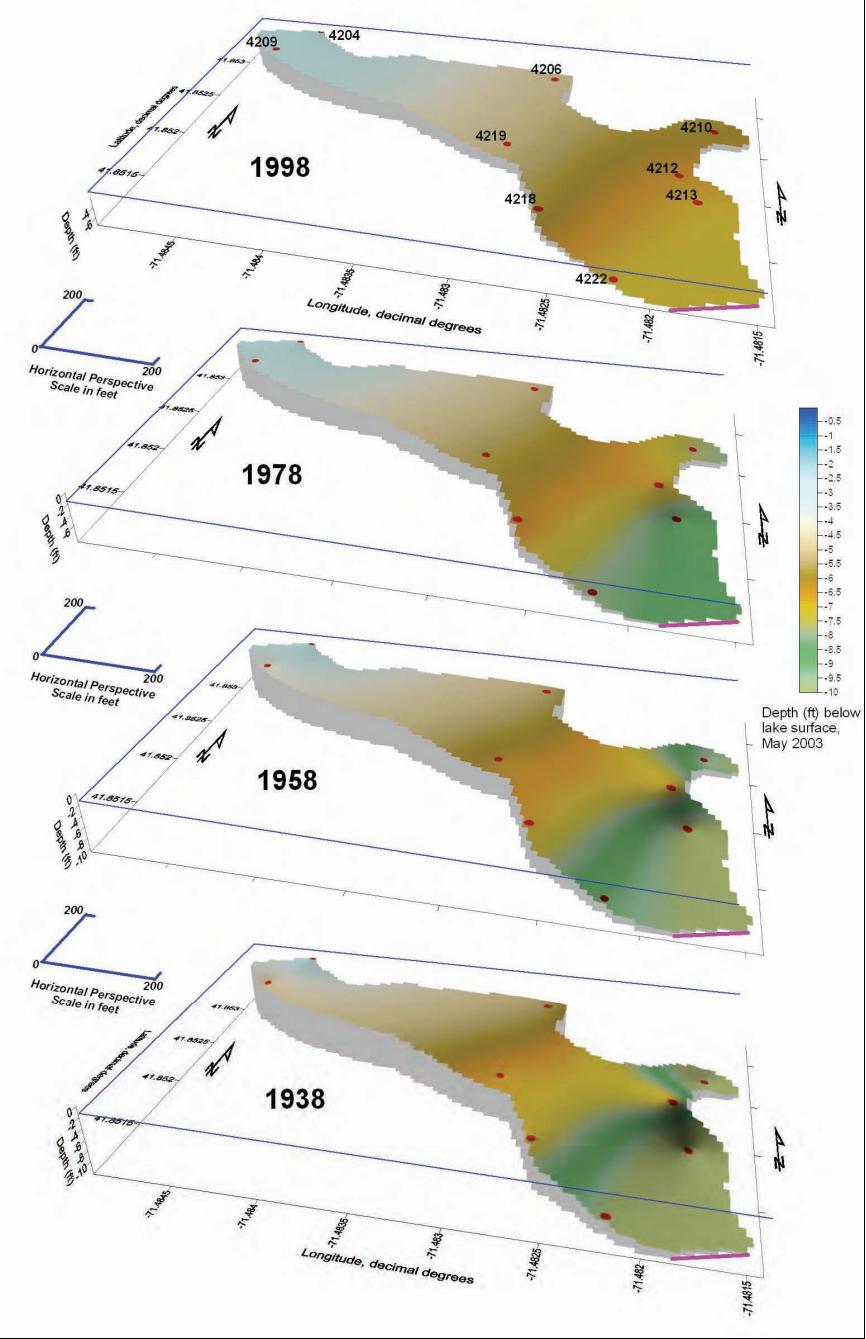


Figure 38. The approximate depth to the bottom of Allendale Mill Pond (sedimentation surface) derived from the CF:CS ²¹⁰Pb model. Data are not available for vibracores CMS-SD-4210 and CMS-SD-4213 in 1938 and 1958 and for vibracore CMS-SD-4222 in 1938.

The highest sedimentation rate in Allendale Mill Pond of 0.092 ft/year calculated from the CF:CS model and 0.087 ft/year averaged from the CRS model occurred in CMS-SD-4210, a vibracore taken in a cove close to a residential area on the right ascending bank of the river. A high sedimentation rate is expected at this location given the isolation of the cove from the main channel flow.

Higher levels of elemental sulfur are found in Allendale Mill Pond than in Lyman Mill Pond and may indicate the presence of elemental sulfur from the powder mill explosion. However, additional explanations addressed for the high levels of elemental sulfur at the Greystone Mill site are applicable to Allendale Mill and Lyman Mill Ponds as well.

Lyman Mill Pond

In Lyman Mill Pond, an organic muck layer ranging in thickness from 11.0 in. to 3.2 ft was recovered in the uppermost interval of the core. Because of the gelatinous nature of the organic muck layer, sediment does not accumulate above it but instead continues through the layer until it reaches a solid boundary at the base of the organic muck layer. The layer possesses a strong hydrocarbon odor, but a definite source responsible for the accumulation of this gelatinous material cannot be identified. However, based on information gathered by Stabler (1908), a probable source for this layer was the Lyman Mill. The Lyman Mill, identified by Stabler (1908) as the chief point of pollution on the Woonasquatucket River above the city of Providence, dumped waste liquors from the mill into the river after passing them through a series of reservoirs used supposedly for purification. According to Stabler (1908) the factory wastes are dye water (3,000 to 4,000 gal), piece-scouring and rinsing water (5,000 to 6,000 gal), and wool-scouring liquor (5,000 to 6,000 gal). The procedure for disposing of the wastes is described in the following excerpt from the publication by Stabler (1908):

> Piece scouring suds and dye water in intermittent flow throughout the day are collected in two 9,500-gallon brick cisterns (used alternately), where they are joined at noon and the end of the day by charges of wool scouring-liquor to which slaked lime (50 pounds per day) had been added. These cisterns serve primarily as receiving and mixing basins, but the mixed liquors are also freed there from the coarser and heavier

suspended matters. The cisterns are cleaned once in three weeks, and about 9 cubic yards of sludge removed. This sludge is dumped nearby until excess of water has drained off, and is then carted away. It contains, as shown, by a sample taken from the dump; total solids, 79.7 per cent; volatile solids, 4.5 per cent; fixed solids, 75.2 per cent; fates, 1.4 per cent; and nitrogen 0.12 per cent. It is chiefly sand, wholly unsuitable for fertilizing purposes, and probably cannot be utilized in any way.

From the receiving cisterns, the combined liquors are pumped into the first of a series of four reservoirs. The first of these is cleaned about once in six months, and 15 cubic yards of scum and an equal amount of sludge are removed. The scum from reservoir No. 1 contains 24.1 per cent, total solids; 15.4 per cent, volatile solids; 8.7 per cent, fixed solids; 4.8 per cent, fat; and 0.4 per cent, nitrogen. The sludge contains 29.5 per cent, total solids; 14.1 per cent, volatile solids; 15.4 per cent, fixed solids; 4.2 per cent, fat; and 0.5 per cent, nitrogen.

The four reservoirs are excavations used as sedimentation basins for what was considered in the early 1900s to be a purification process of the waste liquors. Stabler (1908) does not mention the locations of the four reservoirs. After the sludge was passed through the series of reservoirs, effluent from the fourth reservoir was passed through a bank of coarse cinders before discharging into the river. During the nineteenth and early twentieth century, it was not an unusual practice to dump effluent from the mills directly into a river without evaluating the potential adverse effects on sediment quality (Stabler 1908). The point of discharge was into a stagnant pool described as just south of the weir overflow from the Lyman Mill Pond. Because the pool was stagnant, it was thought at the time of mill operations that a considerable sedimentation and bacterial purification took place that eliminated or reduced any adverse effects on the river (Stabler 1908).

The first reservoir was cleaned every 6 months and 15 cu yd of scum and an equal amount of sludge was removed (Stabler 1908). Only slight accu-

mulation occurred in the other three reservoirs. Within a year, a total of 270 cu yd (160 cu yd from the cisterns, 100 cu yd from Reservoir No. 1, and 10 cu yd from the other three reservoirs) of material (scum and sludge) were removed (Stabler 1908). The investigation into the suspected pollution in the Lyman Mill Pond during the early 1900s is summed up by Stabler (1908) as, the situation at Lymansville, treatment of the waste liquors by lime and sedimentation, dilution and sedimentation in the stream basin, and finally dilution by the main stream, makes pollution at that point negligible.

Because of this gelatinous organic layer, there was not enough sediment to support ²¹⁰Pb and ¹³⁷Cs activity for sediment age dating as determined by radioactive analysis. Elemental sulfur levels are lower in Lyman Mill Pond than what was measured in the Greystone Mill soil samples and the Allendale Mill Pond vibracores (Table 10) and are what is expected in a highly organic soil.

Research contributions to science

The introduction of sediment age dating using anthropogenic input and specific event markers from palynological analysis produce observations and results not reported in previous research. In addition to the introduction of new sediment age dating techniques, the use of existing sediment age dating techniques in a riverine environment provided insight into the sediment regime. Results and observations of this research contribute significantly to the advancement of science.

Geomorphology supports sediment age dating by lending insight into the intricate processes and subsequent depositional features formed in a riverine environment. However, for detailed site characterization, additional information on the sediment regime is needed.

Four sediment age dating techniques were used in this research and the limitations for each method are better understood. Two of these, ²¹⁰Pb and ¹³⁷Cs, have been developed over many years of research but application of these radioisotope techniques has been limited to lacustrine or marine environments. This research applied these methods in a riverine-fluvial environment and found that they are viable techniques that can improve interpretation of the sedimentation cycle where there is an opportunity to collect sediment. However, sediment ages derived from the radioisotope

models should be used with caution and considered a broad estimation of sediment ages rather than an exact timeline.

Additional sediment age dating techniques, elemental sulfur and Japanese knotweed pollen, have not been used in previous research to establish a geochronology. Elemental sulfur is part of the complex sulfur cycle and its role in sedimentation processes is not easily understood and interpreted. Although the results of the elemental sulfur analysis are inconclusive in its use as a sediment age dating method, it is possible that a better understanding of varying oxidation rates of elemental sulfur could provide insight into sedimentation cycles. Another component of gunpowder, potassium nitrate, is soluble in water and proved ineffective as an event marker in subsurface sediments.

Japanese knotweed pollen is a viable and valuable event marker when present in subsurface sediment. The invasive plant began in the New England states and is now widespread throughout North America. Because of the regional extent of Japanese knotweed, it can be useful in assessing recent sediment deposits provided it is known when the knotweed was introduced in the region.

Flood frequency analysis was useful in understanding the impact, if any, of high flood events on sediments. The results of the flood frequency analysis coupled with the geomorphic interpretation show that the high discharge rates resulting from hurricanes and high precipitation are not noticeable in the sediment column within this portion of the Woonasquatucket River.

In addition to these significant scientific contributions, specific observations and subsequent contributions were also made in assumptions generally accepted for ²¹⁰Pb models. Previous research has noted that physical, chemical, and biological processes affect ²¹⁰Pb levels but specific chemicals, such as sulfur, that co-exist with or contribute to high ²¹⁰Pb levels have not been studied.

Technology transfer to scientific disciplines

The results of this research have increased the reliability of geochronology with the introduction of event markers. This information is greatly needed as a forensic tool in geologic fields of study for site characterization.

Palynological research has never used Japanese knotweed pollen in sediment age dating techniques. The introduction of this research provides an event marker that can greatly improve stratigraphic and sedimentary interpretation in sediment that supports the Japanese knotweed pollen.

This research also proves that an extensive and exhaustive historical review of study sites is needed to fully understand anthropogenic effects. Without this focus, research results may be inconclusive when assessing the sediment regime of an area.

The contribution of this research to the environmental aspect of site characterization is significant, not only in the scientific field but also in greatly improving mitigation of contaminated sediment. By knowing the geochronology of a site, and the source and period of contamination, sites can be targeted for sediment coring. Fewer cores are needed to identify the spatial and temporal extent of contamination and thereby result in a substantial reduction in the cost of site characterization and subsequent cleanup.

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13. SUPPLEMENTARY NOTES

14. ABSTRACT

The Woonasquatucket River in North Providence, RI, is a postglacial river flowing approximately 18 miles from its headwaters in North Smithfield, RI, to Providence, RI, where it joins the Moshassuck River and enters the Providence River. In 1776, a powder mill was constructed along the river to support the Colonies' efforts in the American Revolutionary War. The powder mill exploded in 1779, sending tons of gunpowder into the river. Subsequently, with the onset of the American Industrial Revolution in the early 1800s, the river also proved an ideal setting for textile mills. Because the mills operated machinery by waterpower, the river was directed into raceways that flowed through the mills. Dams were strategically placed on the river to aid in the diversion. Mill ponds that formed in response to the obstruction substantially altered sedimentation patterns and depositional features.

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14. ABSTRACT

This research studies a section of the Woonasquatucket River in North Providence to assess the impact of these developments on the sediment regime. By using ²¹⁰Pb and ¹³⁷Cs, accepted methods of radioisotope dating used primarily in lacustrine and marine environments, a geochronology of sedimentation is established. However, because the mills predate the validity of these methods (approximately 150 years before present), other sediment dating techniques are needed to establish a geochronology of events prior to mill construction.

Elemental sulfur and potassium nitrate, components of gunpowder, were analyzed in the sediment to determine a historic timeline prior to the nineteenth century. Although soils at the site of the powder mill contain unusually high levels of sulfur, samples taken in areas away from the effects of the powder mill explosion also reveal high elemental sulfur levels. Pollen analysis focusing on the Japanese knotweed, *Polygonum cuspidatum*, an ornamental plant introduced in New England in the mid-1800s, is successfully used in this research as a stratigraphic event marker. These methods, coupled with a geomorphic framework, provide a significant insight into addressing sedimentation patterns in this and other riverine environments.